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ASD TECHNICAL REPORT 61-654

## RESEARCH ON THE FEASIBILITY OF PROPELLANT DETECTION BY INDUCED RADIOACTIVE TECHNIQUES

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WALTHAM, MASS.

DECEMBER 1961

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<p>ASD TR 61-654</p> <p>Tracerlab, Inc., Waltham, Massachusetts RESEARCH ON THE FEASIBILITY OF PRO- PELLANT DETECTION BY INDUCED RADIO- ACTIVE TECHNIQUES, by F. J. Brousaides, R. Bersin, J. C. McCue, et al. December 1961. 74p. incl. illus., tables. 40 refs. (Proj. 7165; Task 716501) Unclassified report</p> <p>The feasibility of detecting small quantities of toxic propellants in the atmosphere by uti- lizing the decay characteristics of radio- active materials was studied. Activation analysis and inverse radioactive tracer tech- niques were used. The latter may be defined as processes in which a constituent to be analyzed undergoes a reaction (or reactions) ( over )</p>	<p>UNCLASSIFIED</p> <p>I. Brousaides, F. J. II. Bersin, R. III. McCue, J. C. IV. Aeronautical Systems Division, Aerospace Medical Laboratory, Wright-Patterson Air Force Base, Ohio V. Contract No. AF 33(616)-7846</p>	<p>UNCLASSIFIED</p> <p>I. Brousaides, F. J. II. Bersin, R. III. McCue, J. C. IV. Aeronautical Systems Division, Aerospace Medical Laboratory, Wright-Patterson Air Force Base, Ohio V. Contract No. AF 33(616)-7846</p>
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*DECEMBER 1961*

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BIOMEDICAL LABORATORY  
AEROSPACE MEDICAL LABORATORY  
AERONAUTICAL SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

## FOREWORD

This report summarizes a feasibility study performed by Tracerlab, Inc., Waltham, Massachusetts, under Contract AF 33(616)-7846. The study was initiated under Project 7165, "Health Hazards of Materials and Radiation," Task No. 716501, "Evaluation and Control of Toxic Chemical Materials."

The project was administered under the direction of Dr. A. Tamas, Chief, Toxic Hazards Section, Physiology Branch, Biomedical Laboratory of the Aerospace Medical Laboratory, Aeronautical Systems Division. Mr. P. Diamond, Toxic Hazards Section, was the contract monitor.

Work on the contract began January 1, 1961, and was completed October 15, 1961.

# ABSTRACT

The feasibility of detecting small quantities of toxic propellants in the atmosphere by utilizing the decay characteristics of radioactive materials was studied. Activation analysis and inverse radioactive tracer techniques were used. The latter may be defined as processes in which a constituent to be analyzed undergoes a reaction (or reactions) which results in the ultimate release of a radioactive tracer gas whose concentration is proportional to the original constituent to be analyzed. Five toxic materials were selected for investigation; they included nitrogen dioxide, hydrazine, unsymmetrical dimethyl hydrazine, boron hydrides, and beryllium oxide. Emphasis was placed upon the use of Kr<sup>85</sup> quinol clathrates for the detection systems. Properly controlled, these systems were found to be selective to a narrow band of redox materials and gave predictable responses to toxic gas concentrations.

PUBLICATION REVIEW



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## INTRODUCTION

The detection and estimation of toxic materials in the atmosphere has for many years presented a challenge to the analyst. As the biological effects of these pollutants become known and as the maximum allowable concentrations are further reduced the need for more effective and sophisticated monitoring devices grow greater.

The current rapid increase in technological developments of the missile age have far outstripped adequate instrumentation and created problems of fuel detection at low level concentrations. In the search for propellants with greater thrust a gamut of fuels have been investigated and exotic compounds are constantly being synthesized. It is not difficult to see how formidable a task it is for the chemist and toxicologist to keep abreast with this situation, to say nothing of anticipating new systems.

Nevertheless, all available methods for analysis are being pursued, and it is hoped that the development of new modalities will begin to narrow the discrepancy between the number of fuels and the corresponding instrumentation.

One of the more recent techniques of analysis, and one with which this report is concerned, involves the utilization of radioactivity. Such techniques as activation analysis and "inverse" radioactive tracing extend the range of trace analysis since the disintegrations of individual atoms can easily be detected with conventional counters and circuitry.

Activation analysis for trace detection is well established though its practice is restricted due to the limited availability of sources producing high fluxes of nuclear particles. However, we may expect to see more use of the method as the number of atomic piles increase.

Inverse radioactive tracing may be defined as those processes in which a gas or liquid constituent to be analyzed undergoes a chemical reaction or series of reactions which result in the ultimate release of a tracer gas whose concentration is proportional to the original constituent to be analyzed. Common practice is to select compounds containing atoms replaceable by radioactive isotopes having convenient half lives and emitting decay particles of beta radiation energetic enough to give reasonable counting statistics.

To develop the potentialities of these radioactive techniques as applied to toxic gas analysis the following study was undertaken. Five typical toxic pollutants were selected for study: nitrogen dioxide, hydrazine, unsymmetrical dimethyl hydrazine, beryllium oxide, boron hydrides.

No limitation was imposed upon the techniques to be used or reactions that were to be studied. Any system that appeared to have merit and might ultimately lead to a useful monitoring device was given consideration. In some instances the approach to be taken was clear due to the nature of the pollutant. For example, beryllium oxide is very refractory and would be expected to undergo few useful chemical reactions; hence, a physical method of detection was indicated.



## NITROGEN DIOXIDE DETECTION

Prior studies of the physical and chemical properties of  $\text{Kr}^{85}$  quinol-clathrate suggested its use for radiological monitoring of nitrogen dioxide.

Clathrates are an extremely interesting group of solid molecular compounds. These compounds are oriented in such a manner as to present cavities within the structure capable of accommodating guest molecules of the proper dimension. The clathration or inclusion of the guest molecule is commonly performed during crystallization. The chemical properties of the clathrates closely parallel those of the host material.

The bulk of study, to date, of clathrate compounds has been on quinol clathrates (refs. 1, 2). This clathrate approaches the composition  $(\text{C}_6\text{H}_6\text{O}_2)_3 \cdot \text{X}$  where X can be most any molecule that is neither too large nor too small. Already prepared have been quinol clathrates containing  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{HBr}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{HCN}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Kr}$ ,  $\text{Ar}$ ,  $\text{Xe}$ , etc.

The  $\text{Kr}^{85}$  quinol clathrate has been given considerable study at this laboratory due to the chemical inertness of krypton and also the favorable properties of the particular radioisotope.  $\text{Kr}^{85}$  emits 0.67 MEV beta particles plus a small gamma component and has a half life of 10.3 years.

Figure 1 depicts a model of the  $\text{Kr}^{85}$  clathrate. The benzene rings have been replaced by connecting rods to simplify visualization. The rings of alternately large and small balls are hydroxy groups holding the cages together through hydrogen bonding.

If the  $\text{Kr}^{85}$  quinol clathrate undergoes a chemical reaction during which the bonds entrapping the  $\text{Kr}^{85}$  are broken then the radioactive gas will be liberated and can be passed into a counting chamber. The counting rate observed will be some function of the reactant gas concentration and will allow a calibration curve to be plotted relating counting rate with gas concentration.

It has been previously found that strong oxidizing gases (e.g.,  $\text{O}_3$  and  $\text{Cl}_2$ ) are capable of releasing  $\text{Kr}^{85}$  from the clathrate (ref. 3). It was expected that  $\text{NO}_2$  might behave similarly since it also has strong oxidizing properties.

In this study bottled nitrogen tetroxide from Matheson Company was used and diluted successively with purified nitrogen until the desired concentration was reached. A portion of the diluted gas was directed through the  $\text{Kr}^{85}$  quinol clathrate and then through a counting cell which consisted of an end window Anton pancake Geiger tube. A water bubbler was included in the system to allow adjustments in the relative humidity of the gas stream. Figure 2 is a photograph of the apparatus used.

Though bottled  $\text{N}_2\text{O}_4$  was used as a source of  $\text{NO}_2$  supply the presence of the dimer was not of concern since it can be shown from kinetic treatment that  $\text{N}_2\text{O}_4$  is incapable of existence at concentrations of which we will be mainly interested during this study, i.e.  $< 100$  ppm.

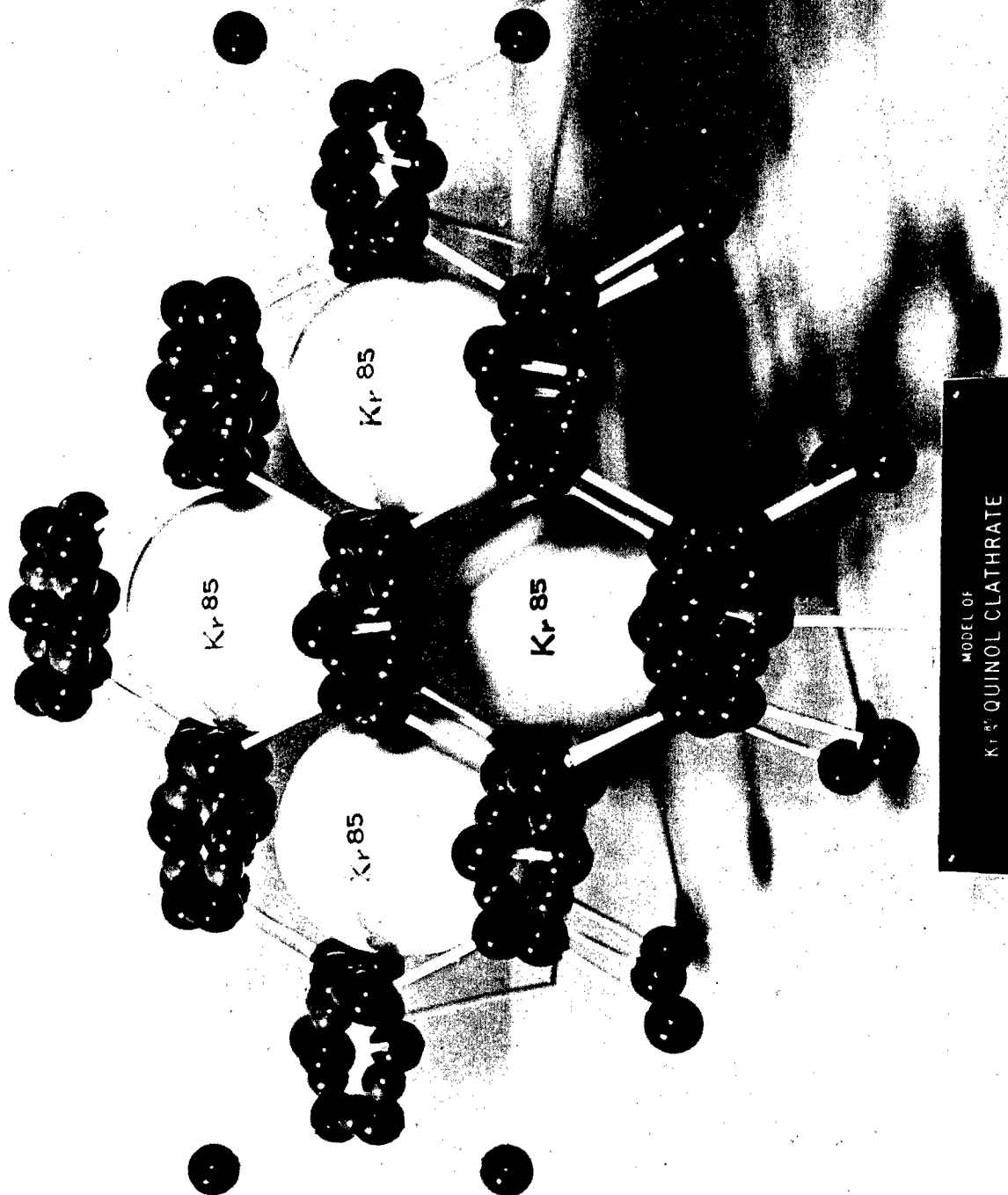


Fig. 1 Model of Krypton-Quinol  
Clathrate

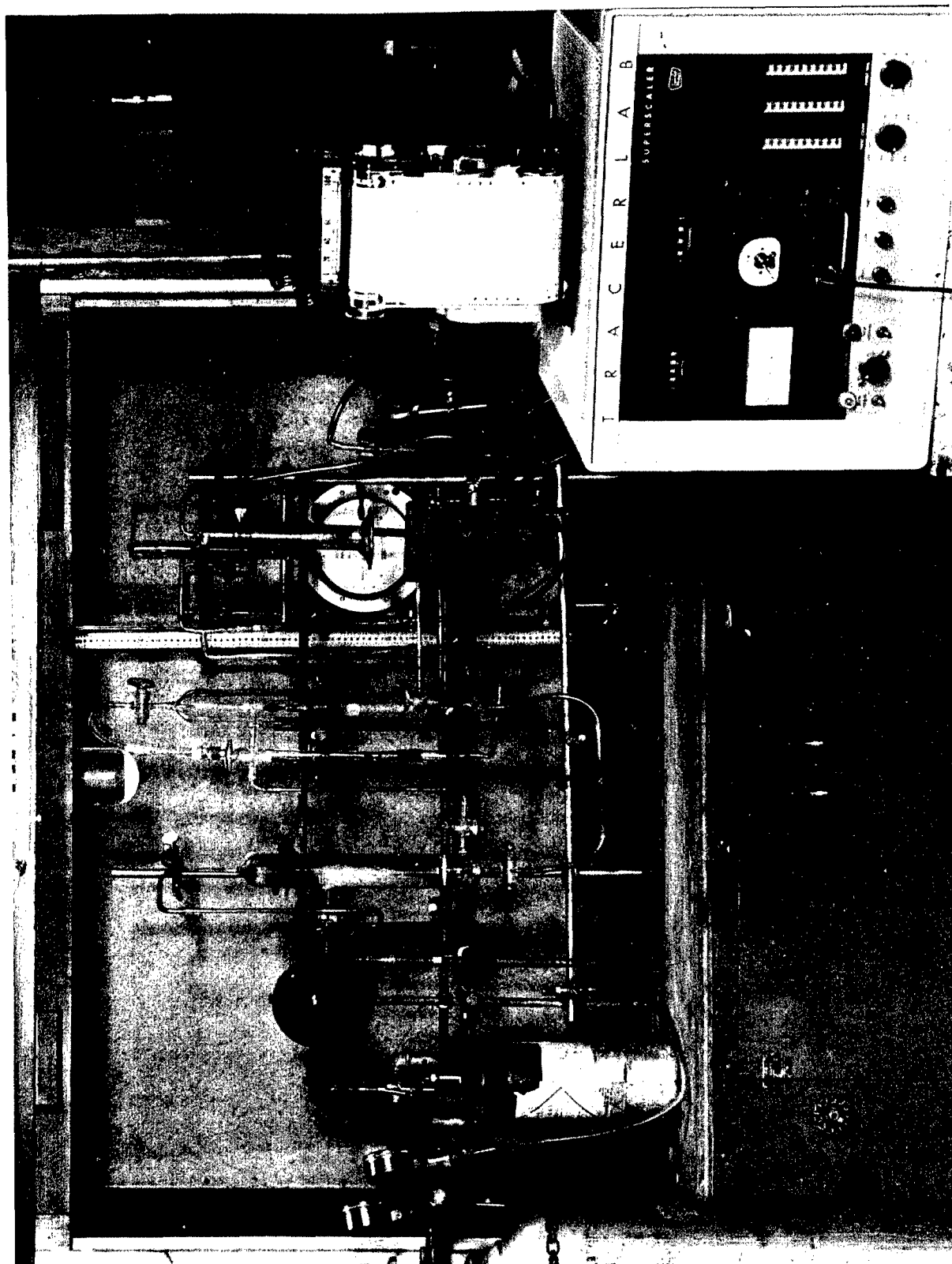
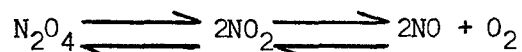


Fig. 2 Experimental Set-up for NO<sub>2</sub> Study

The oxides of nitrogen are closely related in dynamic equilibrium according to the relation,



Thus, we see that  $\text{NO}_2$  in turn can dissociate into nitric oxide, however, this conversion is negligible at room temperature.

Where necessary  $\text{NO}_2$  gas concentrations were calibrated using the spectrophotometric method of Saltzman (ref. 4). Generally, this calibration was performed on the  $\text{NO}_2$ - $\text{N}_2$  mixture from the first dilution reservoir. Then a range of concentrations could be generated by diluting this further with nitrogen, thus obviating continual gas analysis. This procedure was usually satisfactory since absolute calibrations of  $\text{NO}_2$  concentration are not warranted at this point.

The clathrate cell employed had a specific activity of 0.26 mc/mg and weighed approximately 50 mgs.

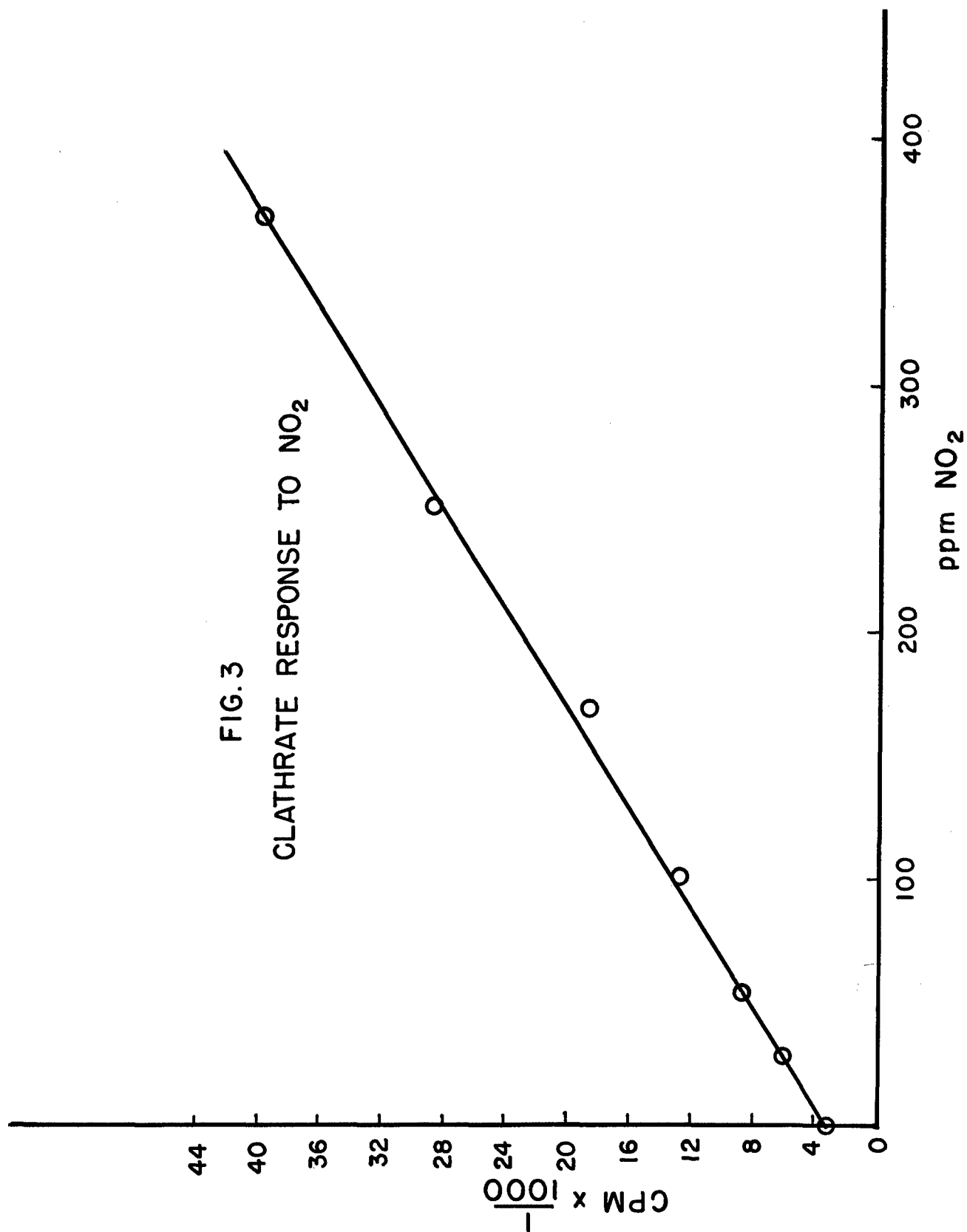
In the first study the response of the clathrate to nitrogen dioxide in dry nitrogen was examined. The sensitivity observed was not very high, 100 ppm  $\text{NO}_2$  giving little more than 10,000 cpm. A typical plot under these conditions is shown in Figure 3 (gross counting rate shown).

A strong reaction dependence upon humidity was found. By varying the ratio of dry nitrogen to wet nitrogen the desired relative humidities were obtained. Relative humidity values stated refer, of course, to values with nitrogen, not air, and at ambient temperature conditions.

At an arbitrary concentration of 34 ppm  $\text{NO}_2$  the count rate was studied as a function of relative humidity. A sharp increase in sensitivity to  $\text{NO}_2$  was observed above 20% R.H. See Figure 4. Operating under controlled humidity conditions it should be relatively simple to achieve part per million analyses. Little data was taken at high humidities as the backgrounds become appreciable due to dissolution of the quinol clathrate. Background values for the above data are as follows.

<u>% R.H.</u>	<u>Background K cpm</u>
60	2.3
50	1.7
40	0.4
30	0.4
20	0.4
10	0.4
0	0.4

FIG.3  
CLATHRATE RESPONSE TO NO<sub>2</sub>



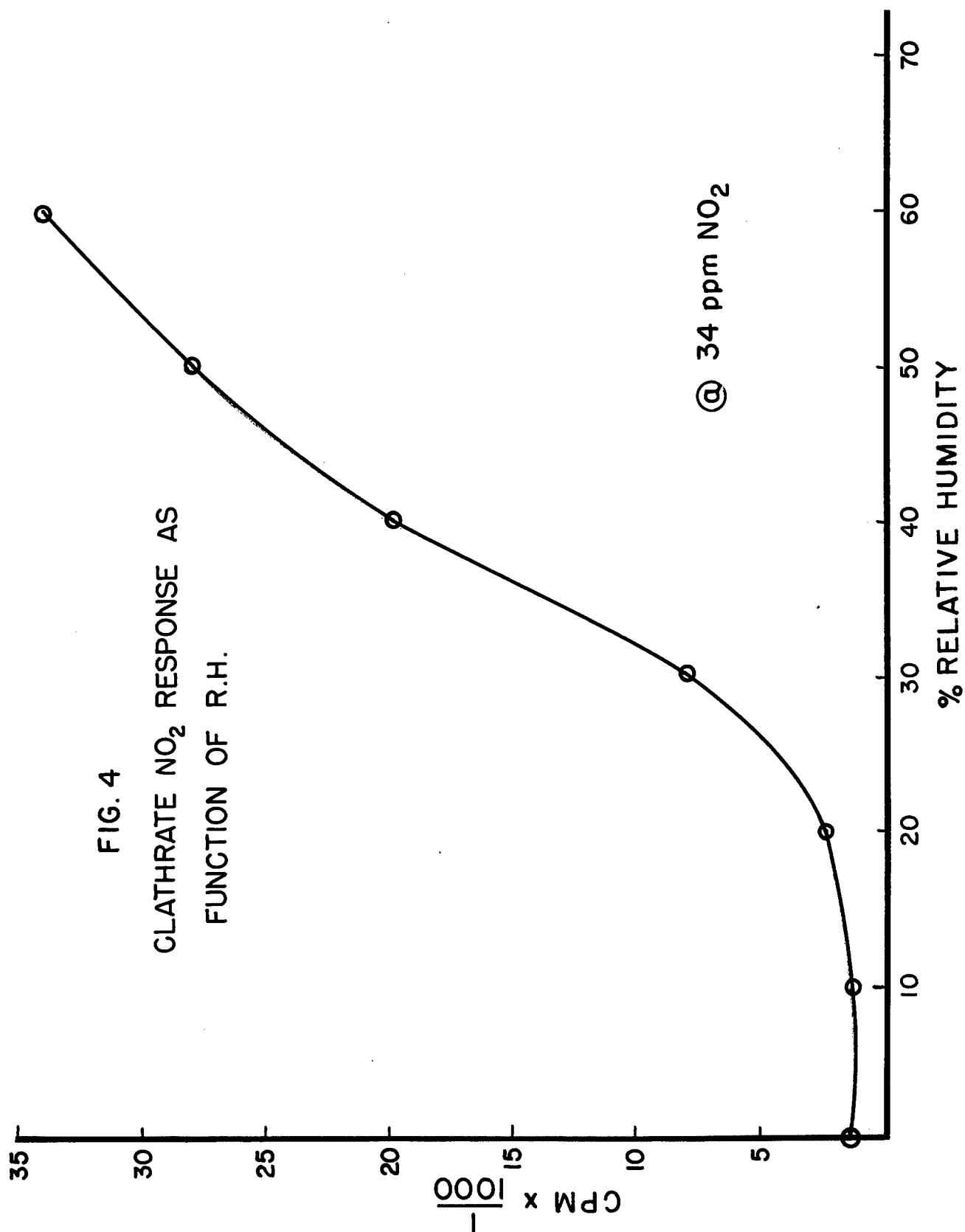


FIG. 4  
CLATHRATE  $\text{NO}_2$  RESPONSE AS  
FUNCTION OF R.H.

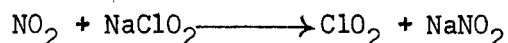
@ 34 ppm  $\text{NO}_2$

It is often difficult to determine exact humidity backgrounds. When moist nitrogen (air) is passed through the clathrate, a relatively high counting rate is initially observed, which decays to some lower value, and upon prolonged exposure the rate will drop even farther. It may simply be that longer time periods are needed to obtain constant steady-state counting backgrounds.

The response of the clathrate to changes in  $\text{NO}_2$  concentration were found to be more sluggish than desired. Ten to fifteen minutes were found to be required for 100% change. A 75-80% change occurs during the first 3-5 minutes.

It was felt that if the  $\text{NO}_2$  could be converted into a gas more reactive with the clathrate, this response time lag could be reduced.

$\text{ClO}_2$  is known to be very reactive with quinol clathrate and in fact provides the basis for Tracerlab's  $\text{SO}_2$  monitor ( $\text{SO}_2 + \text{NaClO}_2 \longrightarrow \text{ClO}_2$ ). Fortunately  $\text{NaClO}_2$  was known to liberate this gas through reaction with  $\text{NO}_2$ . This is the basis for a commercial process for  $\text{ClO}_2$  manufacture (ref. 5).



Considerable data has already been accumulated on the response of clathrate with  $\text{ClO}_2$ . Steady-state counting rates to changes in concentration occur within 3-5 minutes with this system and initial response occurs within 30 seconds.

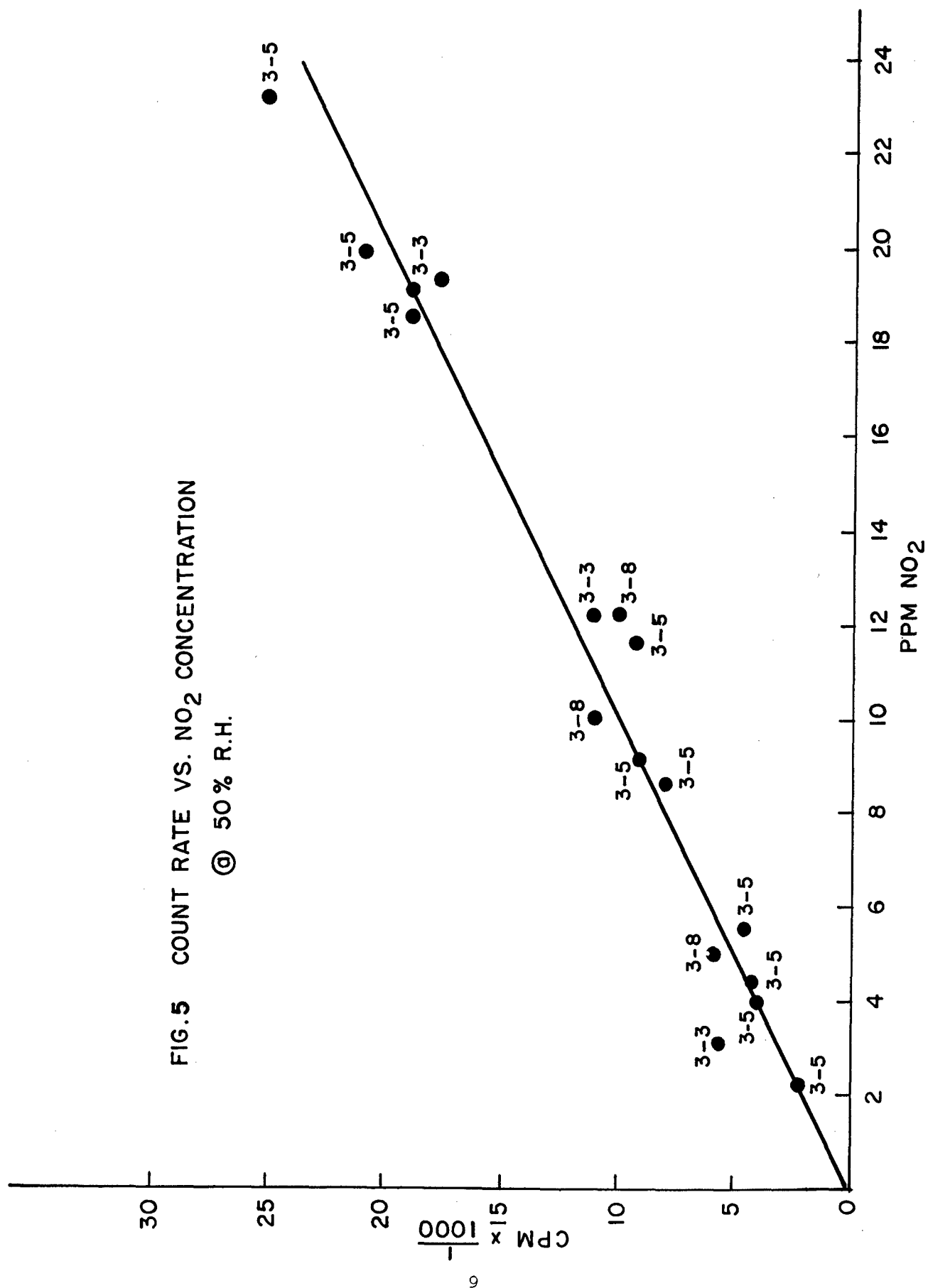
Experiments using the clathrate cell in conjunction with a  $\text{NaClO}_2$  cell indeed confirmed that the reaction proceeded sensitively.

The results of measurements taken over a five-day period are shown in Figure 5. Within measurement errors the system is quite linear. The errors are associated with uncertainties in  $\text{NO}_2$  concentration arising from flow meter readings and dilution errors. The statistical errors are small because of the high counting rates. It should be noted that if 5 ppm is taken as one MAC, the corresponding counting rate of 5000 cpm is approximately ten times the normal background of the system. Thus, the detection of one MAC is well within the operating characteristics of the system.

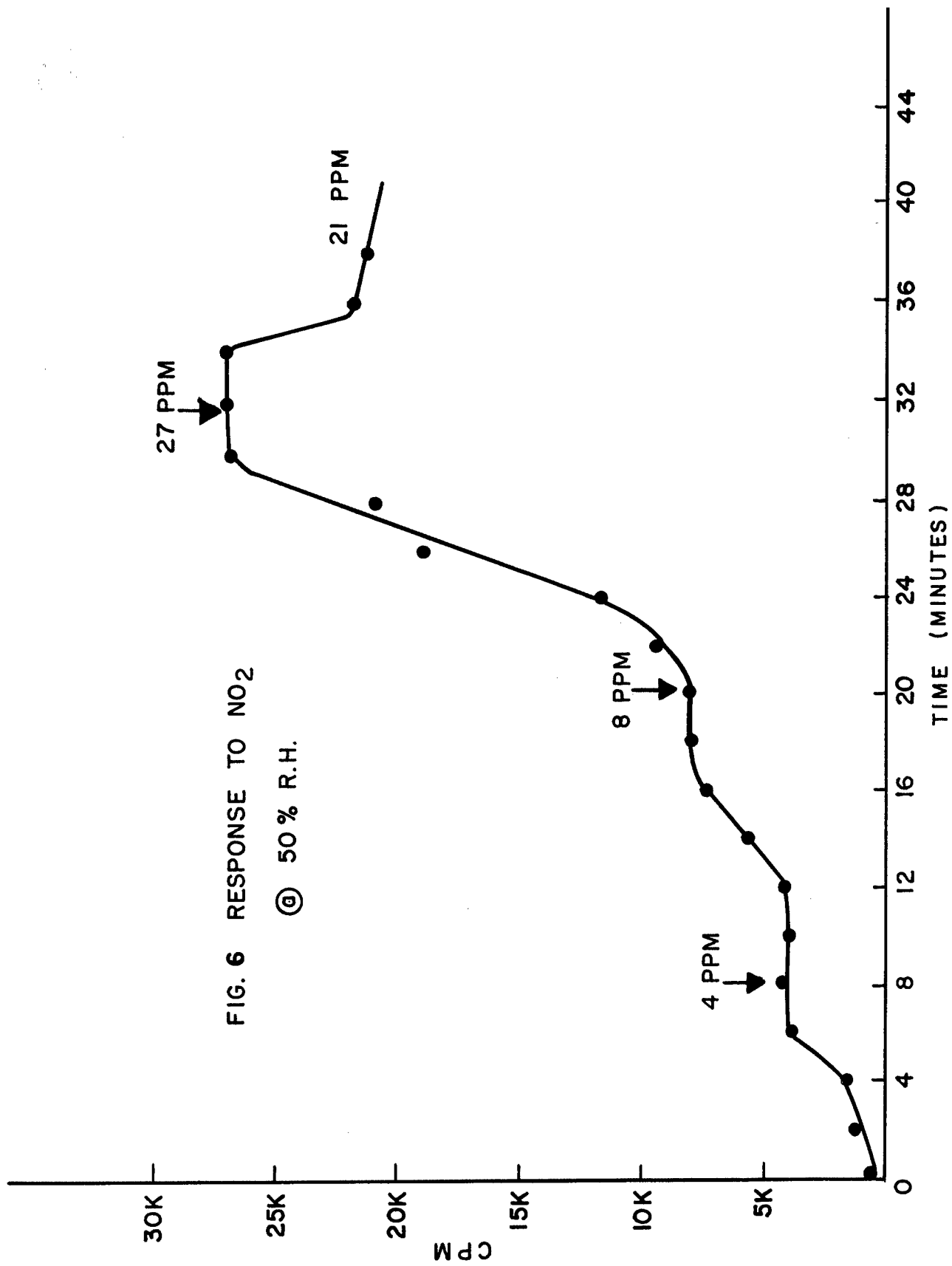
The response of the double release system ( $\text{NaClO}_2$ -clathrate) to changes in  $\text{NO}_2$  concentration is shown in Figure 6. Plateaus represent steady-state counting rates for given  $\text{NO}_2$  concentrations. The arrows represent points at which the concentration was changed. Instant response is almost immediate and the time to reach new steady-state values has been improved, generally requiring five minutes. For greater changes in concentration up to ten minutes were needed. It may be possible to further reduce this time lag by selecting a more satisfactory flow rate through the clathrate. This is an area that can be given more study.

It was felt necessary to study the effect of nitric oxide on both the clathrate and the double release systems since the bottled  $\text{N}_2\text{O}_4$  was used unpurified. In any event, it would be desirable to establish the possible

FIG.5 COUNT RATE VS. NO<sub>2</sub> CONCENTRATION  
 @ 50% R.H.







interfering effect of any specie to operation of the device as an NO<sub>2</sub> monitor.

A platinum heating coil was inserted into the system in front of the clathrate cell. By thermally decomposing the NO<sub>2</sub>, the effect on the count rate could be observed. Since recombination of NO with O<sub>2</sub> proceeds via a third order reaction it is sufficiently slow so that there will be little concern over NO<sub>2</sub> build-up prior to passage through the clathrate. Operating at approximately 3 ppm NO<sub>2</sub> the coil was periodically turned off and on and the effect was noted on the rate meter. With a cold coil the count rate was 33 K cpm, with a hot coil the rate dropped slowly to below 10 K cpm after 6 minutes.

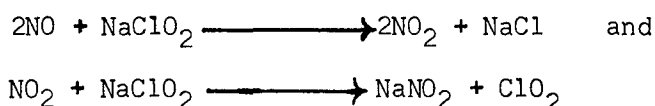
It was difficult to decide whether or not all of the NO<sub>2</sub> had been converted and that the slow decrease in count rate merely reflected a slow response of the clathrate or whether some NO<sub>2</sub> was passing through the coil unaffected. Certainly the latter could be possible since the complete dissociation of NO<sub>2</sub> would necessitate evaluation of optimum conditions of temperature, coil geometry, flow rate, etc.

A chemical analysis of the gas mixture showed that the coil as used was 98% effective in converting the NO<sub>2</sub>. Thus, the relatively high count rate noted above with the coil in operation either reflected sluggish clathrate response or was due to an increased background due to the passage of heated gas through the clathrate.

An experiment then was performed using bottled nitric oxide instead of the tetroxide. An arbitrary concentration of 100 ppm nitric oxide was established and upon analysis for NO<sub>2</sub> content was found to contain about 2 ppm of that gas.

The count rate of this mixture when passed through clathrate yielded 2.5 K cpm at a relative humidity of 60%. This is a count rate of the order of magnitude we would expect for 2 ppm NO<sub>2</sub> at that humidity. It now appears likely that nitric oxide does not react with clathrate and that any counts may be attributable to NO<sub>2</sub> impurities.

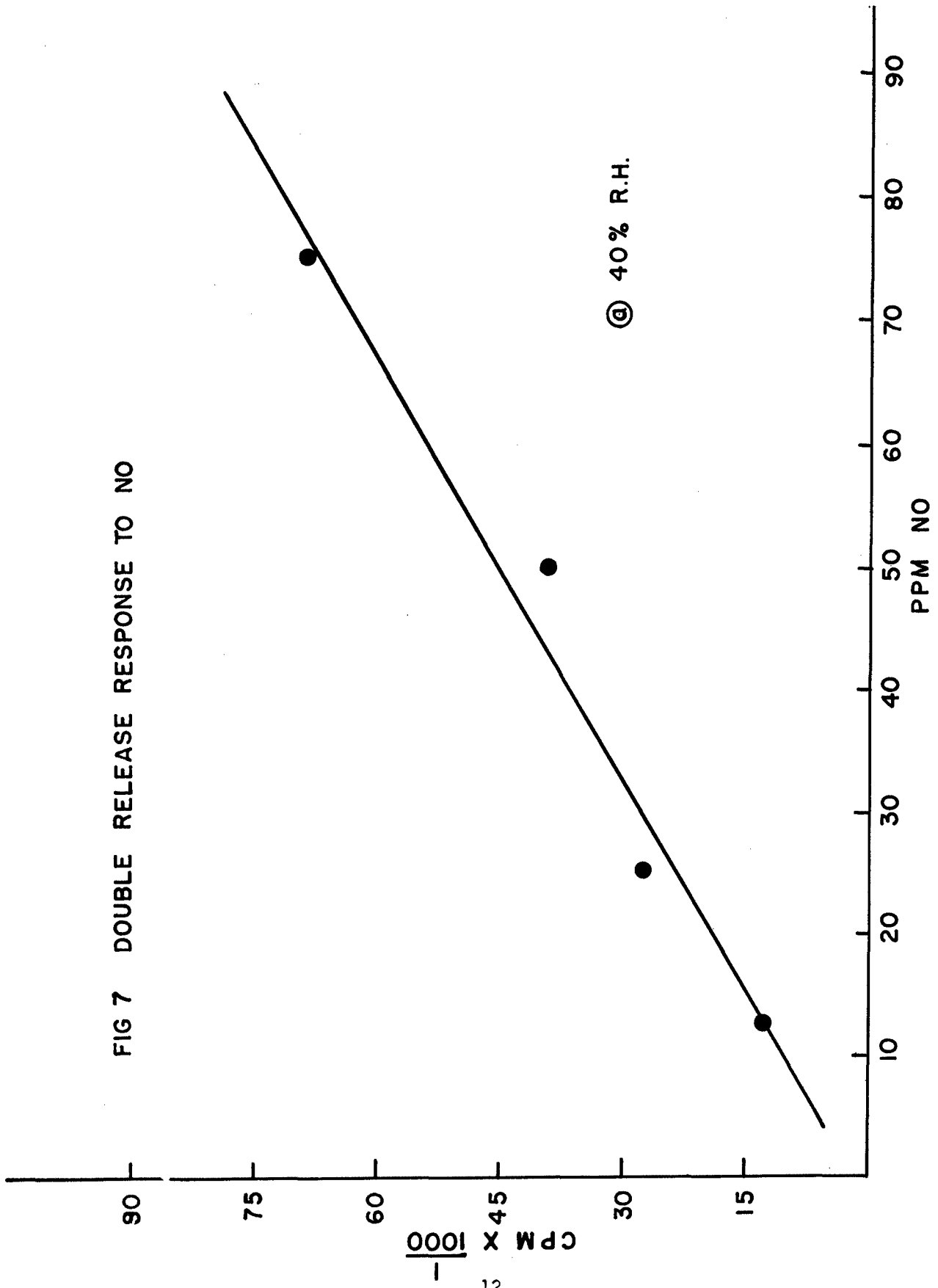
It was believed that nitric oxide would also react with the double release system to release Kr<sup>85</sup>. The work of Riolo (ref. 6) showed that both nitric oxide and nitrogen dioxide reacted exothermically with NaClO<sub>2</sub> to release ClO<sub>2</sub>. The process proceeded both in solution and with dry NaClO<sub>2</sub>. The reactions are reported to proceed with high efficiency. The reactions are as follows:



Response of the double release was found as expected with nitric oxide, Figure 7.

The relative response of NO<sub>2</sub> and NO with the double release systems would be an experimental test of the above reactions. Using tank N<sub>2</sub>O<sub>4</sub> the

FIG 7 DOUBLE RELEASE RESPONSE TO NO



@ 40% R.H.

response to arbitrary  $\text{NO}_2$  concentrations was determined. Using the same "set-up" the responses to NO was found by thermally decomposing the  $\text{NO}_2$  gas stream by the use of the platinum coil. In this manner the necessity for using two independent flow systems and different bottled gases was eliminated as was the need for rigorous analytical calibration of the gas mixtures. See Figure 8. The correlation is good so that the chemical reactions at the sodium chlorite cell probably do proceed at very high efficiencies.

Table I summarizes the affects of  $\text{NO}_2$  and NO on the single and double release systems.

TABLE I  
SINGLE AND DOUBLE RELEASE RESPONSES TO  $\text{NO}_2$  AND NO

	<u>Clathrate</u>	<u><math>\text{NaClO}_2</math> + Clathrate</u>
$\text{NO}_2$	Yes	Yes
NO	No	Yes

Thus, we see that the differential response of the single release system will allow the  $\text{NO}_2$  concentration of the gas stream to be selectively detected while the total response of both gases can be measured with the double release combination.

When  $\text{NO}_2$  is to be monitored in the presence of ozone, the latter can be destroyed by a hot coil which will also convert the  $\text{NO}_2$  to NO. The NO will be detected by double release.

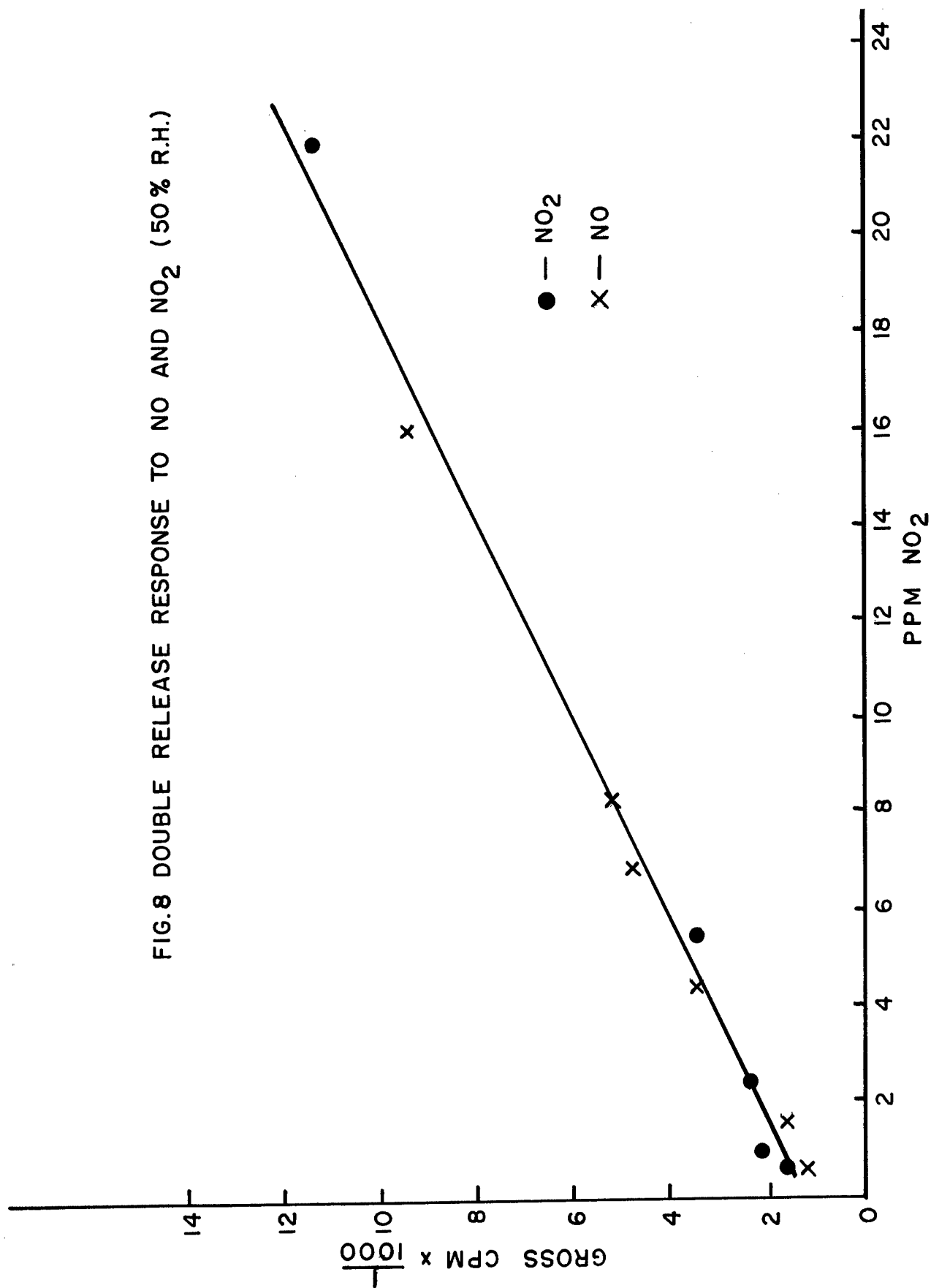
#### DETECTION AND DETERMINATION OF HYDRAZINE AND UNSYMMETRICAL DIMETHYL HYDRAZINE

Both of these compounds will be discussed together due to their similarity in chemical behavior. Generally, the properties of the hydrazines involve their strong reducing capabilities. This is true in spite of the fact that from potential data the hydrazine couple should exhibit strong oxidizing abilities to any great extent.

In selecting a reaction suitable for use in radiological detection, the following properties were sought. The reactant compound should be a solid and have a low vapor pressure at ambient temperatures and must liberate a gaseous reaction product (or volatile vapor) which can be tagged with a useable radioisotope.

Practically all the reactions examined were immediately rejected as unsuitable since there was either no gaseous by-product or the gaseous product was nitrogen or ammonia. Nitrogen has no long-lived radioisotope and cannot be used as a tracer.

FIG.8 DOUBLE RELEASE RESPONSE TO NO AND NO<sub>2</sub> (50% R.H.)



Several reactions that were considered included:

- a)  $2\text{N}_2\text{H}_4 + \text{K}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{HN}_3 + \text{NH}_3 + \text{K}_2\text{SO}_4 + 3\text{SO}_2^* + 4\text{H}_2\text{O} + \text{O}_2$
- b)  $\text{N}_2\text{H}_4 + 2\text{S}^* \longrightarrow \text{H}_2\text{S}^* + \text{N}_2$  (ref. 7)
- c)  $\text{N}_2\text{H}_4 + \text{tagged aldehydes} \longrightarrow [\text{H}_2^*\text{O}]$
- d)  $\text{N}_2\text{H}_4$  clathrate systems

One feature of hydrazine chemistry was particularly intriguing and immediately suggested itself as a method of analysis. Since it does not involve radiochemical techniques and could not be justified under the scope of the contract, little more than a cursory examination of it was made. It utilized the fluorescent properties of azines compounds. For completeness the conclusions from this examination will be included in this report.

#### Fluorescent Detection of Hydrazine

Aromatic aldehydes react with hydrazine to form colored compounds. One sensitive spot test for hydrazine utilizes salicylaldehyde and claims are made for concentrations down to 2 ppm (ref. 8).

These reactions are often quantitative and provide spectrophotometric methods for hydrazine analysis. The method used for calibration of hydrazine concentrations in gas stream during this study utilizes, in fact, the color of one of these azines (ref. 9).

In addition, many of these azines are highly fluorescent compounds which permit the detection of hydrazine to be pushed to high limits. Both salicylaldehyde and p-dimethylaminobenzaldehyde have been reported as being the basis for highly sensitive tests for hydrazine (refs. 10, 11). With the latter reagent a detection of  $5 \times 10^{-10}\text{g}$  of hydrazine at a dilution of  $10^8$  was claimed. Nitrates, nitrites, ammonium salts, azides, and strong reducing agents do not interfere.

It was felt that a reagent impregnated paper strip method would be convenient and adaptable to continuous monitoring. The device would also lend itself readily to portability and simplicity of design.

Limited use of this technique, for example, has been made with other air pollutants. Hydrogen sulfide has been detected with lead acetate sensitized paper (not fluorescent method) and a fluorescent method for fluoride detection using paper has been reported (ref. 12).

A few experimental tests were made in an effort to determine if such a method was applicable to the fluorescent detection of hydrazine.

Filter paper circles were treated with an acidified solution of p-dimethylaminobenzaldehyde. These circles when dried were put into a special holder which was inserted into a gas stream containing low hydrazine concentrations. A 4 ppm hydrazine gas stream passing through the test paper produced detectable amounts of fluorescent compound in less than one minute

(at 50 ml/min flow rate). The fluorescent compound was observed visually upon irradiation with a portable mineral lamp.

No quantitative measurements were taken so that nothing can be said of fluorescent intensities as a function of hydrazine concentration or of reproducibilities. Work was discontinued at this stage.

We feel that this technique warrants further study. It is unquestionably sensitive and if proved to be interpretable and free from major interferences it should be a significant method of hydrazine analysis.

#### Single Release Clathrate System

Considerable work has been performed here with Kr<sup>85</sup> quinol clathrate as an air pollutant detector. It is the policy at this laboratory to continually evaluate the response of different compounds with clathrate alone and in conjunction with multiple release systems. In this manner a "catalog" of clathrate responses can be compiled which will also serve to define the extent of interference by a given compound to the monitoring of another and the conditions under which response will be found.

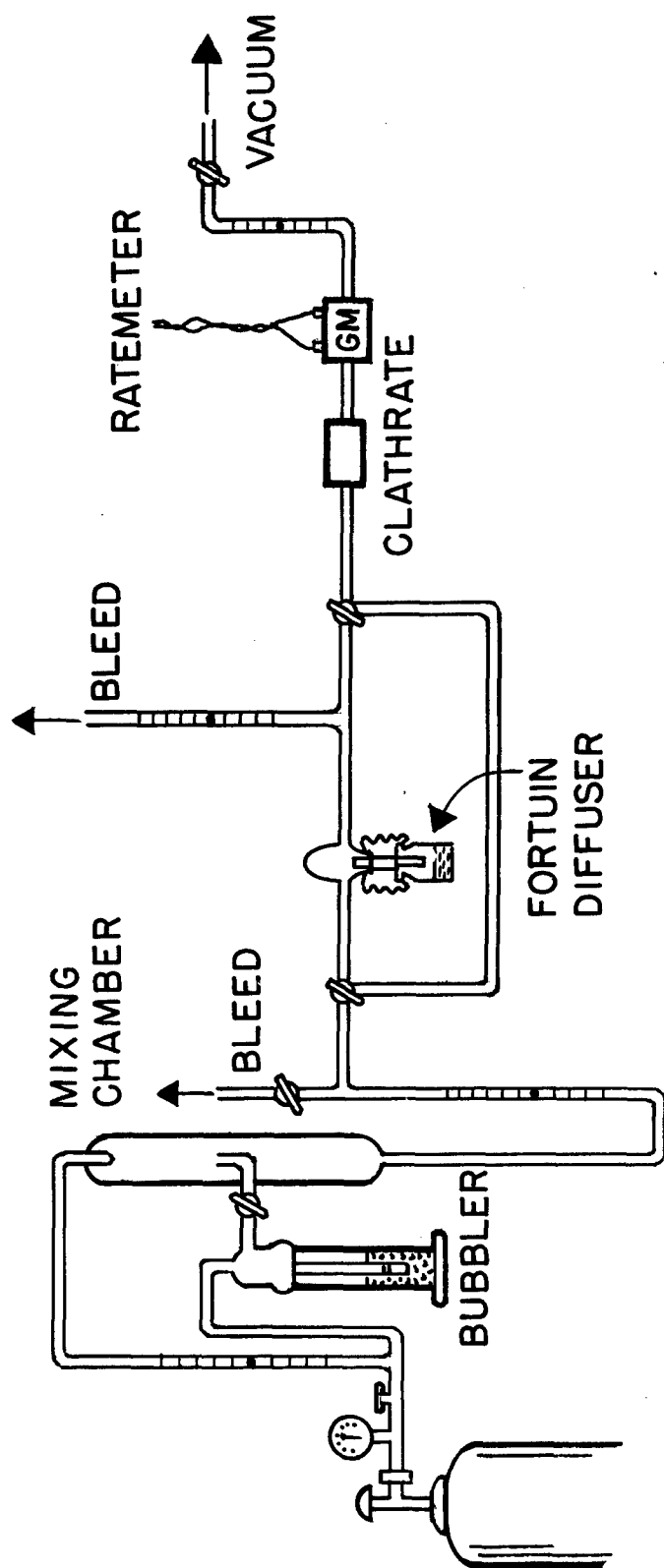
In preparing gas streams containing requisite concentrations of vapors, such as hydrazine, the method of Fortuin (ref. 13) was adopted. This simple and convenient method depends upon the diffusion characteristics of a vapor in a cell whose exit is restricted by a capillary to leak out at a controlled rate into a gas stream. The rate of leak is dependent upon cell geometry, which is a constant, certain physical properties of the compound, and the ambient temperature. This leak rate can be calculated or determined experimentally. Figure 9 depicts the arrangement used. It may be noted that allowances for controlling the relative humidity of the gas stream were made by mixing dry gas with moist gas.

The output of the diffuser was calibrated colorimetrically using p-dimethylaminobenzaldehyde as the reagent (ref. 9).

The response of the clathrate to a concentration range of 0-20 ppm hydrazine was studied as a function of relative humidity. It was found, surprisingly, that clathrate did react with hydrazine and with good sensitivity, Figure 10.

Using dry nitrogen, hydrazine was found to behave erratically with the clathrate and reproducible results could not be made. When moisture was provided the reaction began to settle down and was more predictable. Though moisture appears needed for reaction stabilization, the same degree of dependence on humidity was not found as with that seen with nitrogen dioxide.

With NO<sub>2</sub> there is a sharp increase in sensitivity with increasing relative humidity, while with hydrazine the response appears to plateau above 30% R.H. Figure 11 is a replot of the Figure 10 data values for 40 and 50% R.H. response in which region the variability was minimized. Even if the humidity was not controlled (humidities above 50% were not studied) the errors certainly would not be gross.



DYNAMIC FLOW SYSTEM FORTUIN DIFFUSER

FIG. 9



FIG 10 HYDRAZINE DETECTION WITH CLATHRATE

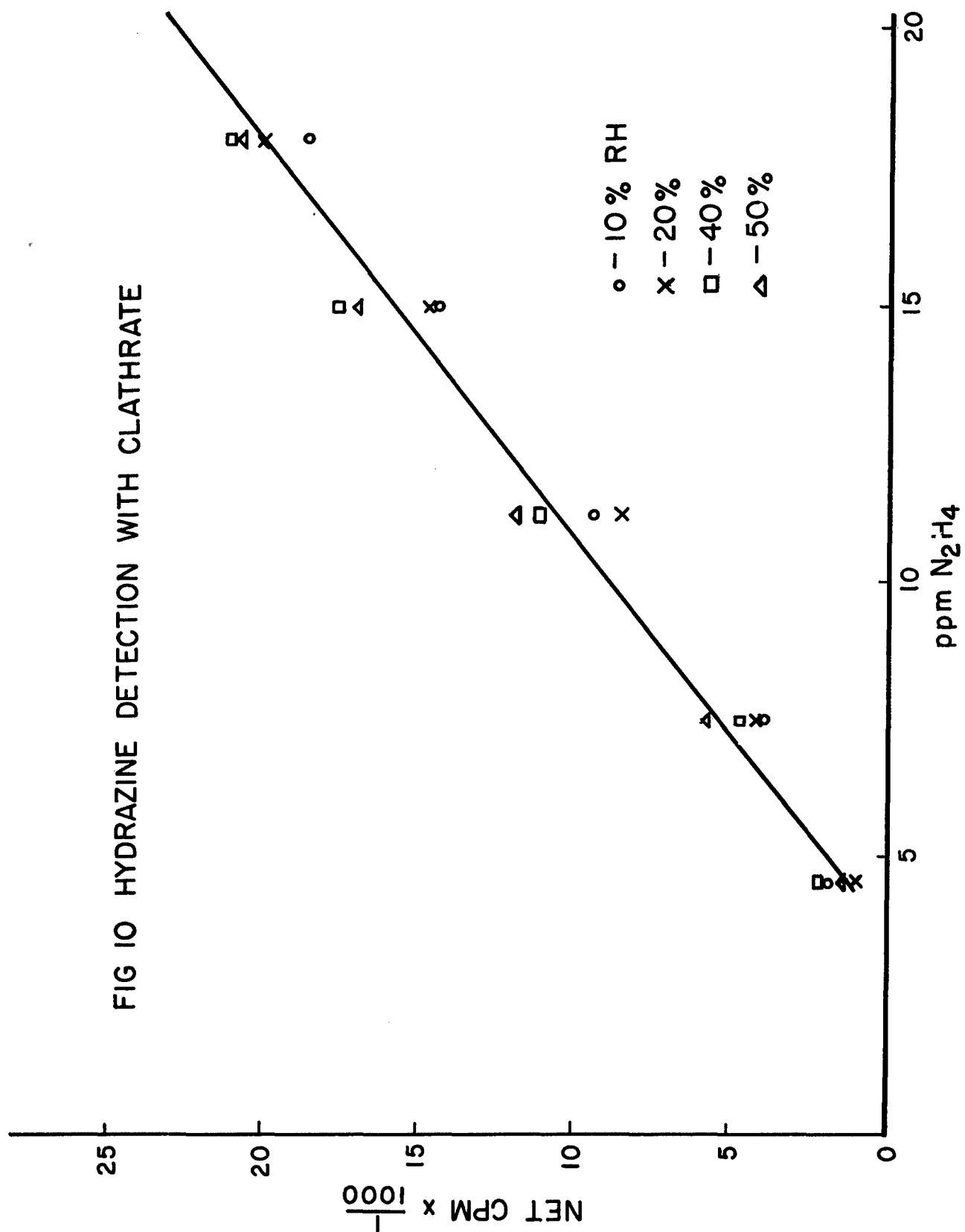
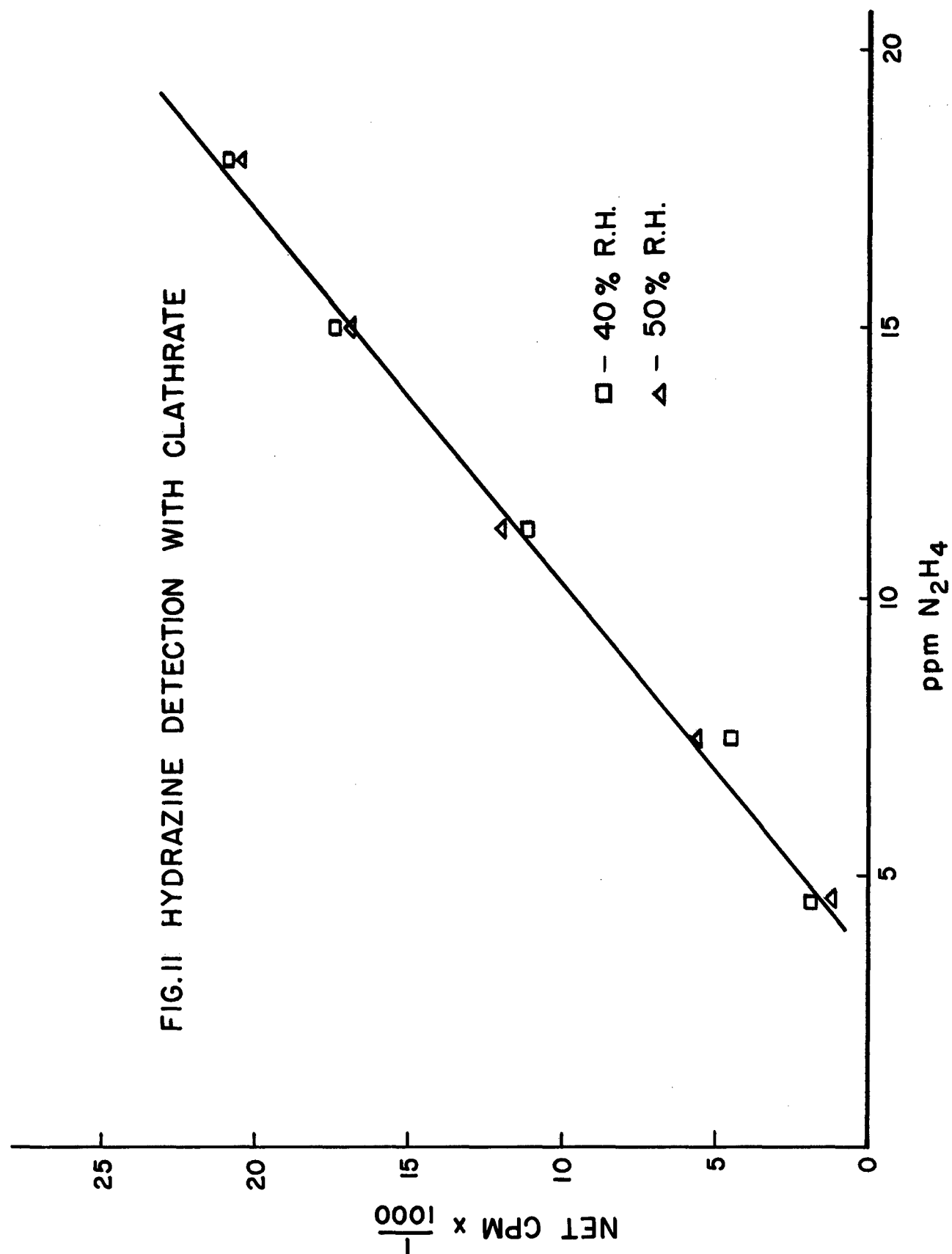


FIG.II HYDRAZINE DETECTION WITH CLATHRATE

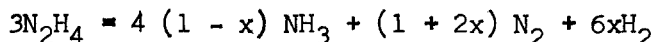


The recovery times to new steady-state concentrations were from 2-4 minutes. In general, this reaction appeared "clean". The relative response of quinol clathrate appears to be comparable for both  $\text{NO}_2$  and  $\text{N}_2\text{H}_4$  when humidities are high. However, the response of  $\text{NO}_2$  is reduced drastically at humidities below 30%.

Dimethyl hydrazine also reacts with the quinol clathrate but the sensitivity is very much less than found with hydrazine. Also, the response is very erratic and unreproducible.

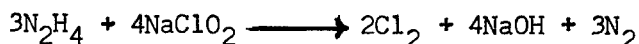
Since the clathrate responds to both  $\text{NO}_2$  and the hydrazines, means must be provided to allow differentiation if clathrate is to be used as a sensor.

It was previously established that a heated coil placed in the gas stream would convert  $\text{NO}_2$  to  $\text{NO}$  which when passed through a "double release" combination would give a response similar to  $\text{NO}_2$  directly with clathrate. By passing hydrazine across the hot coil, we should be able to thermally destroy it to yield non-reactive by-products. A general equation for hydrazine decomposition is given by Audrieth and Ogg (ref. 14).



Nitric oxide would be unaffected and would be detected by the double release mechanism. Hydrazine in turn could be estimated by subtracting the above  $\text{NO}_2$  response from a total response of  $\text{N}_2\text{H}_4$  and  $\text{NO}_2$  found by direct clathrate monitoring.

Time did not permit the study of the hydrazines with the  $\text{NaClO}_2$  - clathrate system. It is interesting to speculate, however, on the likelihood of such a reaction. Hydrazine being a strong reducing agent might be expected to react with  $\text{NaClO}_2$  to yield chlorine.



It is known that chlorine is strong enough an oxidizing agent to release krypton from the clathrate. This is definitely an area for investigation.

#### Reaction with Elemental Sulfur and a Modified Double Release Clathrate System

The reaction



was considered for the direct monitoring. The feasibility of this reaction was first tested with non-radioactive sulfur.

If the reaction proceeded to an extent which would make it useful for hydrazine monitoring the liberated  $\text{H}_2\text{S}$  could be detected by our  $\text{SO}_2$  monitoring system after the  $\text{H}_2\text{S}$  had been converted to  $\text{SO}_2$  by passage across a hot coil. If the results were encouraging, the next step was to prepare a sensor cell using  $\text{S}^{35}$  and to study the direct reaction.

The following block diagram illustrates the arrangement used in the preliminary study.

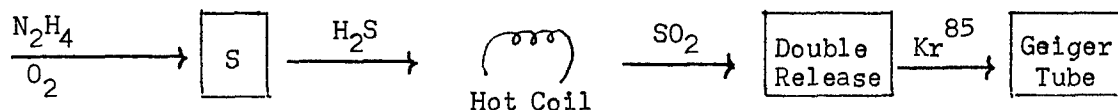


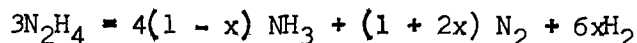
Figure 12 is a plot of data taken at 50% R.H. The sensitivity and linearity were surprisingly good considering the multiplicity of cells used. These results appeared to substantiate the reaction feasibility so that preparation of a tagged sulfur cell seemed warranted.

A cell containing 67 mg of  $S^{35}$  containing a total activity of approximately 10 millicuries. The cell was coupled directly to the Geiger tube and obviated the double release section of the system.

Repeated attempts to get response with this cell using concentrations of hydrazine up to several hundred parts per million failed. This was extremely perplexing in view of the sensitive response previously found using the double release to detect the  $SO_2$ .

Re-examination of the earlier experiments led to the following conclusions. The hydrazine was passing unreacted through the sulfur cell and was catalytically converted to NO at the hot platinum coil. The nitric oxide has previously been shown to be detectable by the double release system.

The reactions at the platinum coil probably include first a thermal decomposition,



followed by platinum catalysis,



The second reaction is a step in the commercial preparation of nitric acid.

It has previously been established that ammonia will not react with either the single or double release systems so that any contribution from this source to the counting rate can be discounted.

To check the validity of some of these conclusions, a series of quick experiments were performed. The experiments would also help to define the conditions under which response would be expected. Table II summarizes the conditions of the test and the observed response.

FIG.12 RESPONSE OF SULFUR TO  $N_2H_4$   
WITH  $SO_2$  DETECTION

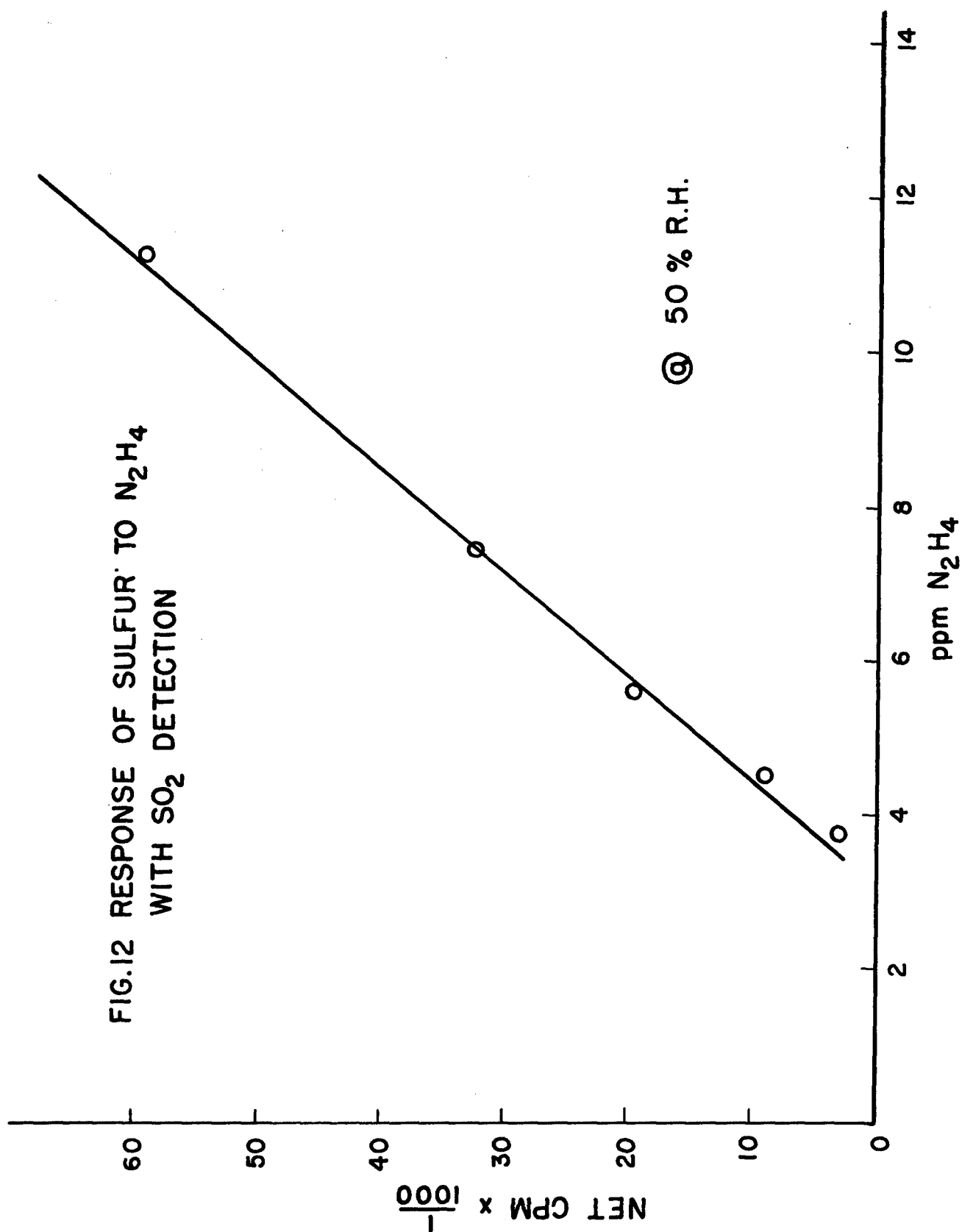


TABLE II  
RESPONSES UNDER SPECIFIED CONDITIONS

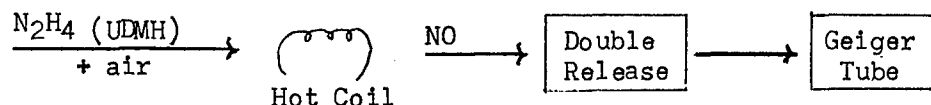
<u>Reaction Conditions</u>			<u>Response</u>
UDMH + air	→ ( ) →	Double Release	Yes
UDMH + N <sub>2</sub>	→ ( ) →	Double Release	No
UDMH + air	→ ( ) →	Single Release	No
NH <sub>3</sub> + air	→ ( ) →	Double Release	Yes
NH <sub>3</sub> + air	→ → →	Double Release	No
NH <sub>3</sub> + N <sub>2</sub>	→ ( ) →	Double Release	Slight + erratic

We can conclude from the above that for double release response with UDMH,

1. Oxygen is required
2. NH<sub>3</sub> itself is not the active agent
3. Decomposition products of NH<sub>3</sub> on Pt are active

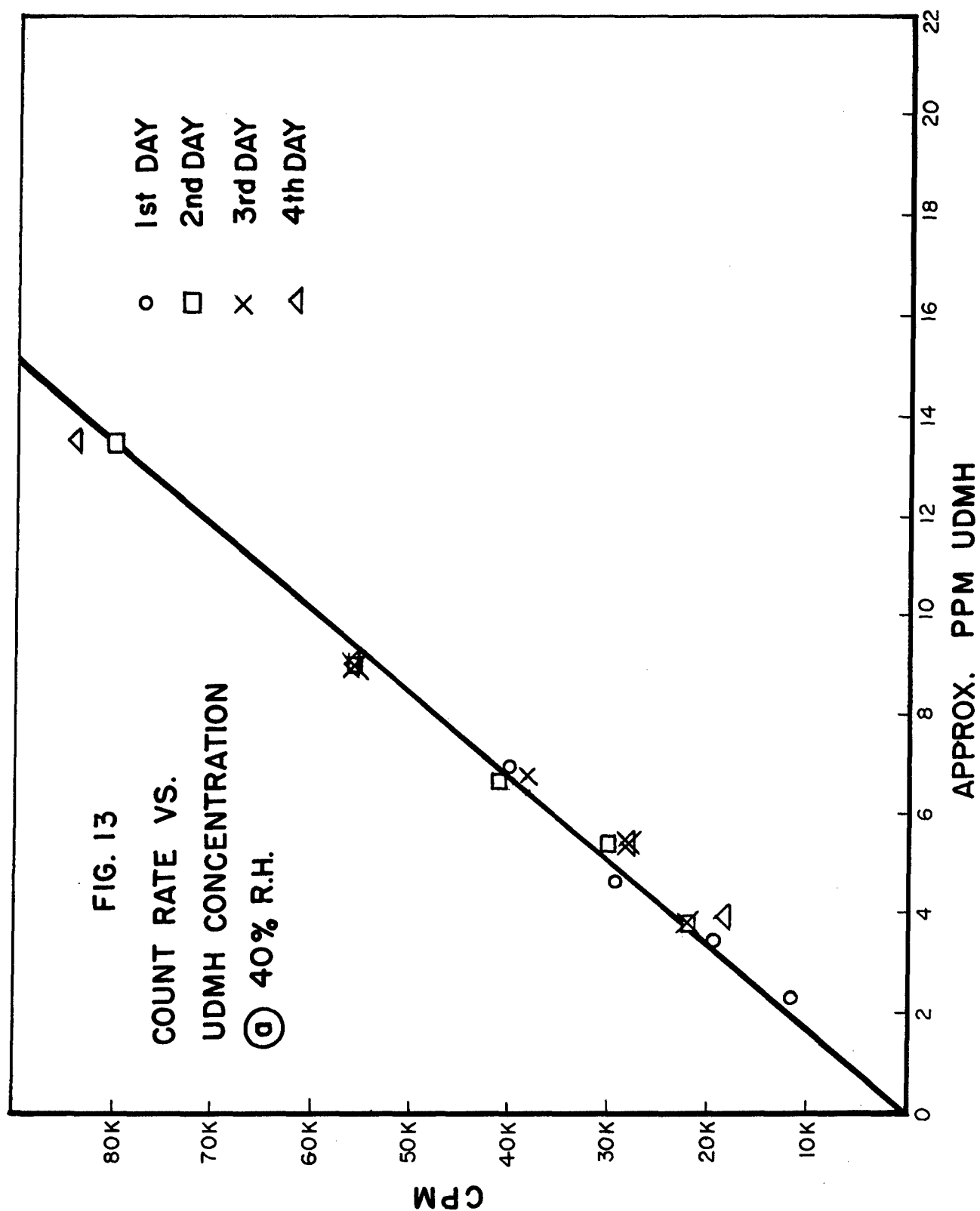
These facts in conjunction with the postulated equations make it appear likely that UDMH is in fact catalytically decomposed to nitric oxide. Of course, one could analyze for the presence of nitric oxide in the effluent gas stream for direct substantiation.

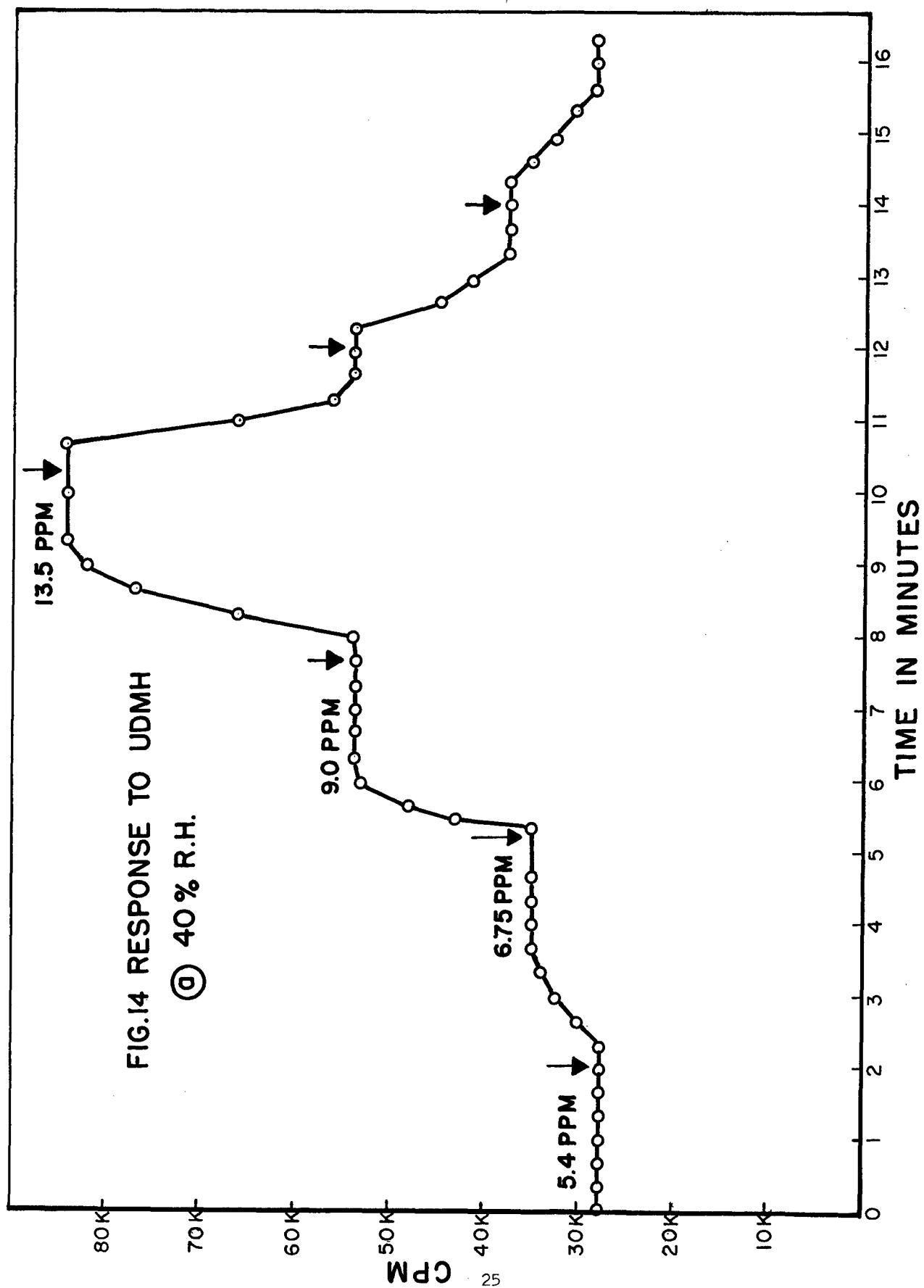
In view of this interpretation the previous experimental set-up was assembled with the exclusion of the unneeded sulfur cell as depicted below.



This arrangement was used with UDMH and was found to give a response similar to that previously found with hydrazine. The precise relative sensitivity of UDMH and hydrazine was not determined due to the uncertainty in UDMH concentration in the gas stream. Figure 13 shows a plot of count rate vs approximate UDMH concentrations taken over a four-day period. The reproducibility is excellent. The response of the system to different UDMH concentrations was seen in less than 30 seconds and steady-state counting rates were reached in 2-4 minutes. See Figure 14. The arrows indicate points at which the concentration of the gas stream was altered.

The dependence upon humidity of the reaction was studied as a function of concentration. Relative humidities of 20, 30, 40 and 50% were studied.





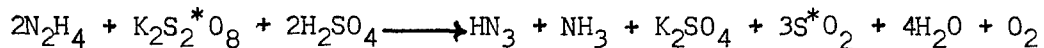


Within each group excellent linearity was found except for the data at 30% R.H. which for unexplained reasons showed a scattering of points. Figure 15.

#### Other Methods

As time permitted, other reactions which appeared promising were given examination.

The reaction described earlier involving the interaction of hydrazine with tagged persulfate, i.e.

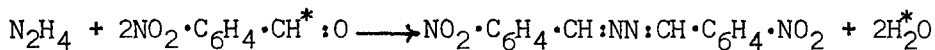


while interesting howed little promise of success since persulfate is known to decompose slowly; hence, the system would probably exhibit a very high background.

The other reaction described in this section was the action of hydrazine on tagged aldehydes with the liberation of tritiated water. For use in a monitor the tagged solid compound would be inserted in the flow path of the gas to be analyzed. The tagged by-product of reaction, water, would be liberated then swept into an ionization detection chamber. If the water is not desorbed rapidly from the tagged solid a heater coil might be necessary to promote this release.

To test the feasibility of such a reaction for hydrazine monitoring, two organic aldehydes were selected for study and were tagged with tritium using the Wilzbach method of tritium exchange. The compounds used were p-nitrobenzaldehyde and 2,4 dimethoxybenzaldehyde. The resulting specific activities were found to be 14.2 millicuries/g and 62.5 millicuries/g respectively.

The reactions expected with hydrazine and UDMH with p-nitrobenzaldehyde, for example, are

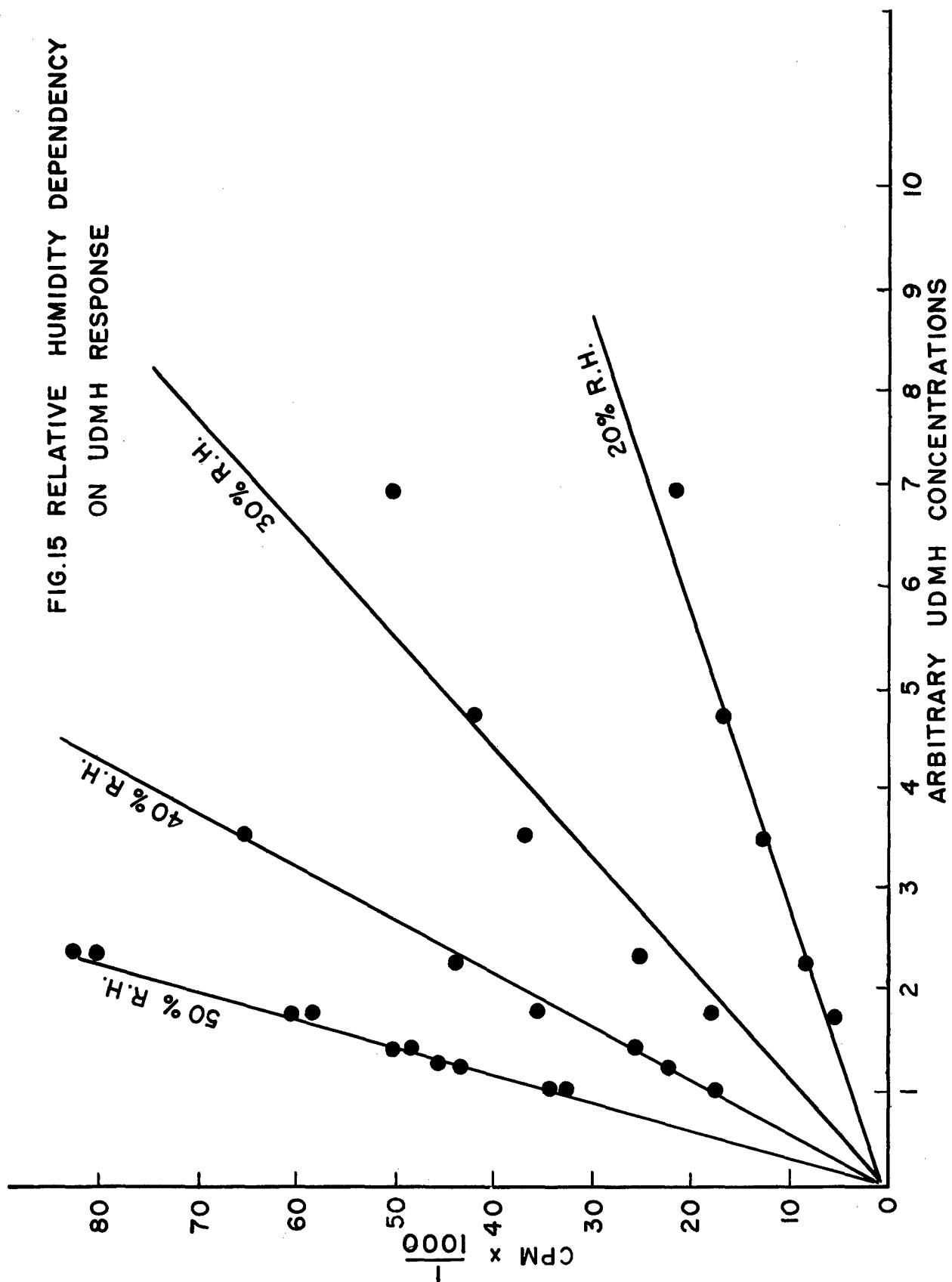


For purposes of this experiment an internal flow G.M. detection system was used. Hydrazine was introduced into the line with the Fortuin diffuser.

When hydrazine free Geiger gas was passed through either compound, a low background ( $\leq 100$  cpm) was observed. The addition of hydrazine to the stream in the ppm range brought about a high counting rate. More visible proof of reaction was in the eventual color change of the tritiated compounds.

Unfortunately, the counter repeatedly became contaminated almost immediately so that no quantitative data could be gathered. The source of contamination is apparently due to adsorption on the counter walls by the tritiated water which is held tenaciously.

FIG.15 RELATIVE HUMIDITY DEPENDENCY  
ON UDMH RESPONSE



Thus, regardless of the chemical reaction efficiency, the technique will be useless unless a counter can be designed which will obviate the contamination difficulty. Conceivably counter walls could be coated with some type of plastic which has less of an affinity for water or an arrangement might be devised whereby the walls could be heated to prevent water adsorption. In any event, activity along these lines of investigation were discontinued.

## DETECTION OF BORON HYDRIDES

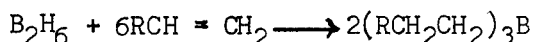
In the search for missile and space vehicle propellents of high specific impulse, the borane fuels have been given special attention (ref. 15). With the exception of hydrogen and beryllium compounds the boranes are unexcelled as high energy fuels.

Typifying the boron hydrides in both physical and chemical properties is diborane which is also a key intermediate to the synthesis of higher boranes and alkylation products. This gas was selected for study since it represented the series.

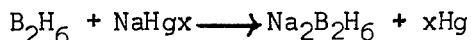
The diborane, as received from the Callery Chemical Company, was diluted with dry nitrogen to approximately 200 ppm. Diluted mixtures of this type were used throughout the investigation. The gas was analyzed for diborane content by conversion to boric acid with subsequent spectrophotometric detection using carminic acid (ref. 16).

The more important types of reactions of the boranes are listed below:

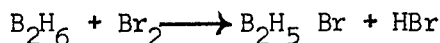
1. Reaction with oxygen yielding a variety of undetermined products.
2. Hydrolysis with water to yield  $H_2 + H_3BO_3$ .
3. Reaction with ammonia (e.g.  $B_2H_6 \cdot 2NH_3$ ).
4. Formation of alkyl and aryl boron compounds



5. Metal derivatives

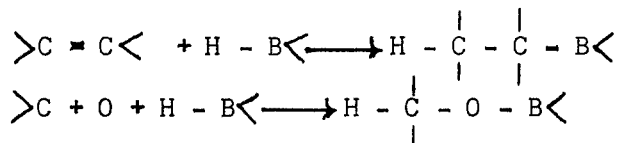


6. Reaction with halogens



7. Grignard reactions

8. Addition to multiple linkages of type





9. Formation of borine compounds of type  $A:BH_3$  such as  $(CH_3)_3N:BH_3$  and  $B_2H_6:2PH_3$

All those reactions which have no gaseous by-products, or involve interaction with liquids or solids of high vapor pressure are not of interest for inverse radiochemical tracer studies. These restrictions are severely limiting. The most promising area appears to be in reactions of boranes with multiple linkages. Brown and Subba Rao have reported that carboxylic acids are rapidly reduced by diborane with the evolution of hydrogen (ref. 17). If the hydrogen is replaced by tritium, there is a possibility of monitoring the borane using ionization chamber detection.

The single and double release clathrate mechanisms will be examined for diborane response in conformance with routine policy.

Reaction of Diborane with Tritiated Carboxylic Acids

Two acids were selected for study, p-nitrobenzoic acid and 3-nitrophthalic acid, and were tagged using the Wilzbach tritiation technique. The specific activities were found to be 11  $\mu\text{c/g}$  and 12  $\mu\text{c/g}$  respectively.

The reactions expected are of the following type;



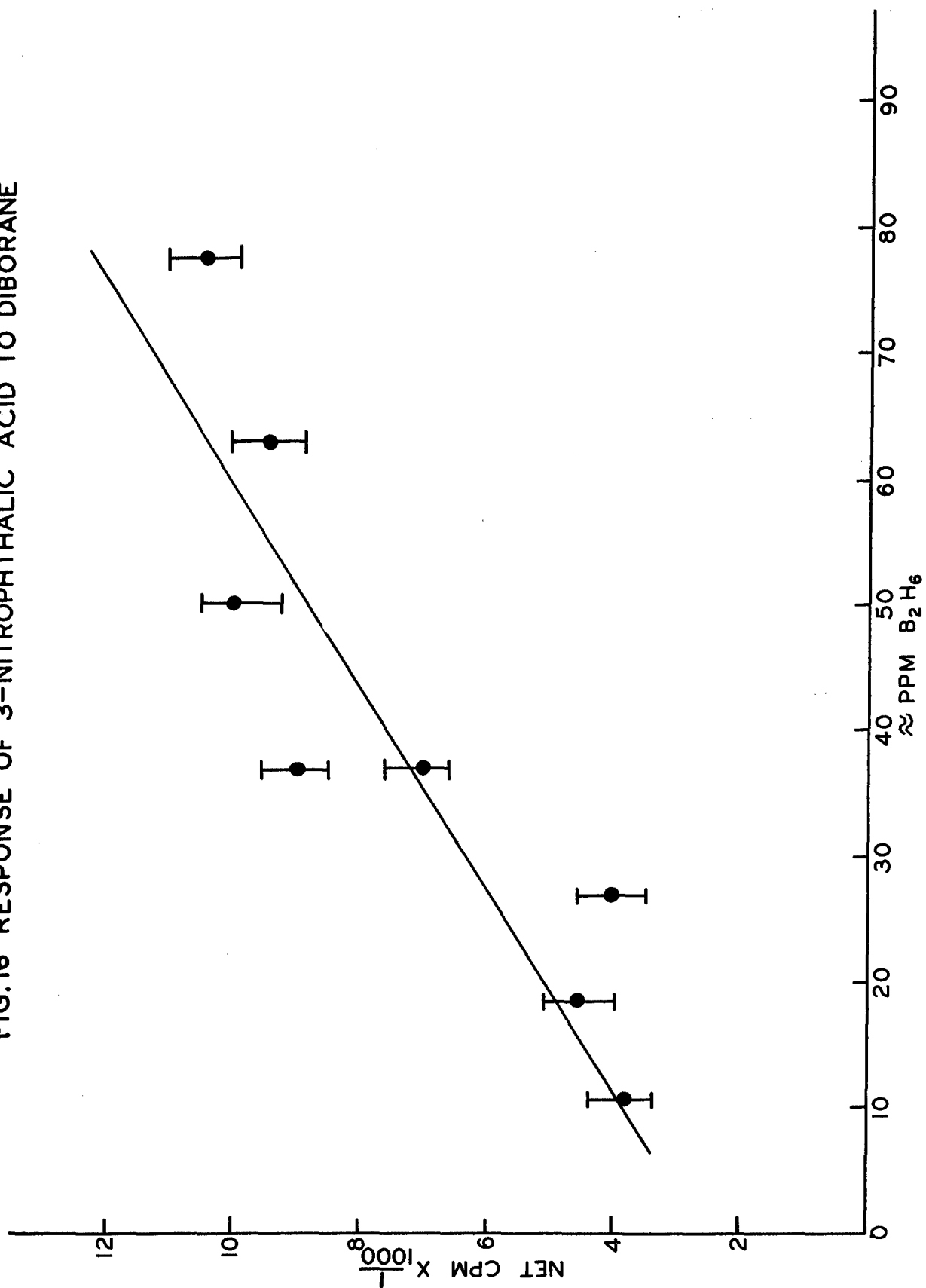
The reactions of acids with diborane were studied by Brown and Subba Rao in a solvent medium of tetrahydrofuran or the dimethyl ether of diethylene glycol (D.G.). The reaction with the tagged material was examined both in solution and as a gas-solid reaction.

The gas-solid reaction was examined first. Diborane in concentrations up to several hundred ppm displayed little reactivity with the tagged acids. For purposes of this study, detection was made with a proportional counting system with the diborane diluted with proportional counting gas (He and  $CH_4$ ).

For the solution study the tagged compounds were dissolved in DG and put into a glass cell into which the gas to be monitored was introduced through a fritted glass bubbler tube. Using pure proportional gas, an extremely high background, over 20 K cpm, was observed, as illustrated in Figure 16. This background made meaningful experiments difficult. Though there was a net counting rate above background using diborane mixtures, the statistical errors were quite large.

The vapor pressures of the acids are probably too low to account for the high background through volatilization. It is likely that the tagged compound contained impurities which were formed during the tritiation process. In the Wilzbach process the compound to be labeled is exposed to an atmosphere of tritium gas for a period of time sufficient to allow the desired degree of exchange between hydrogen atoms. Concurrently, a certain amount of radioactive degradation of the compound will occur. The amount of decomposition will depend upon the compound, amount of activity used,

FIG.16 RESPONSE OF 3-NITROPHTHALIC ACID TO DIBORANE



length of exposure, etc.

It is quite possible, since the tagged acid was not purified, that degradation products are responsible for this background.

Further studies using purified Wilzbach material or the use of compounds that are synthesized directly with tagged components would resolve the feasibility of this type of reaction for radiological monitoring.

#### Single and Double Release Clathrate Study

The single release clathrate system was found not to respond to diborane. Diborane concentrations up to 100 ppm were used with and without humidity with no effect.

To study the effect of diborane on the double release mechanism, an experimental "set-up", similar to that used in the nitrogen dioxide study, was used.

Using a humid atmosphere (43.0% R.H.) response was observed. Figure 17 is a typical plot. Due to the rapid hydrolysis of  $B_2H_6$  with water, the concentrations of that gas at the instant of monitoring is not known. A chemical analysis would not help since the method used here does not differentiate between diborane or its hydrolysis product, boric acid. The concentration values reported were calculated directly from flow meter readings.

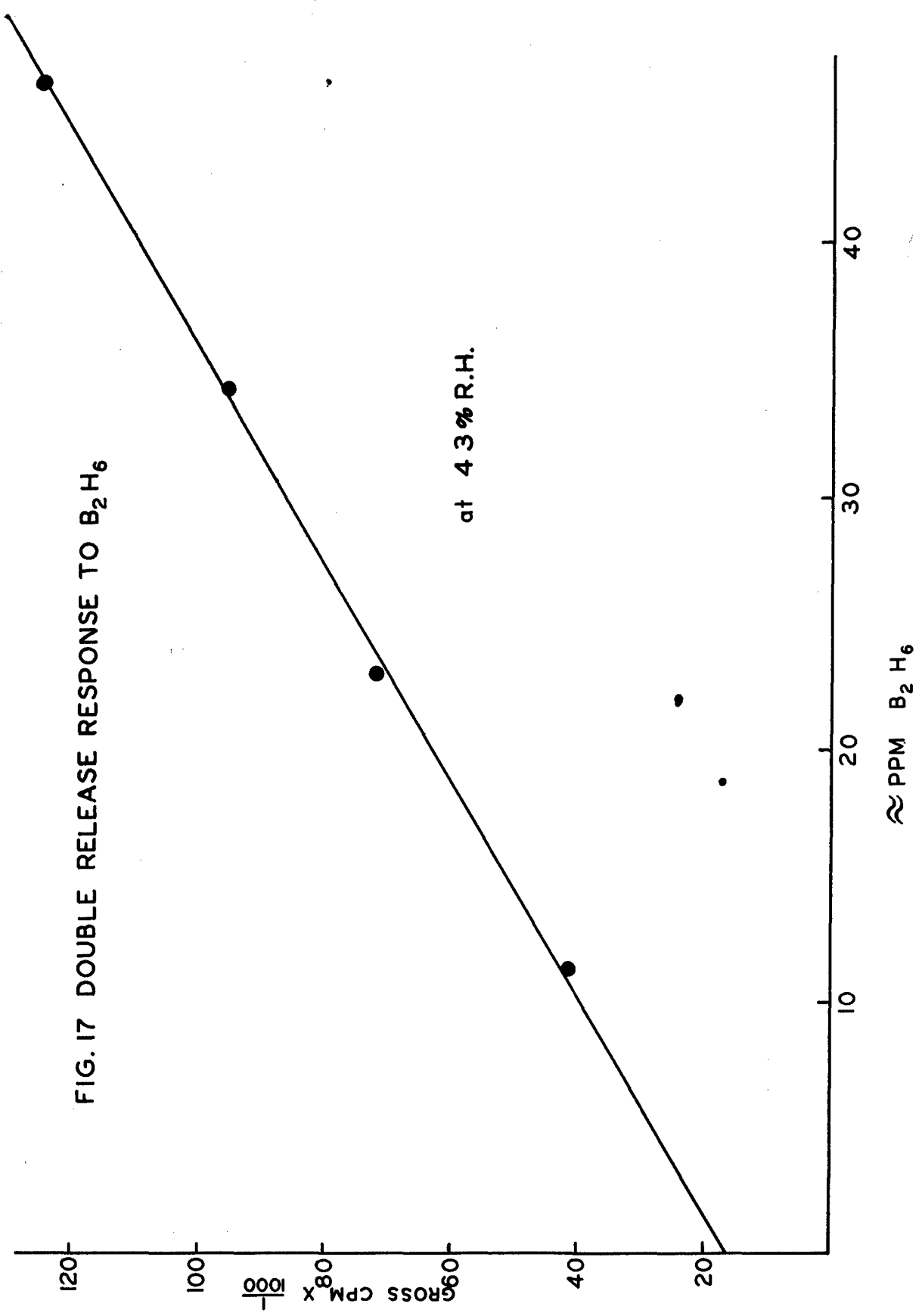
Using higher humidities, a decrease in sensitivity was found which is not what would be normally expected. Undoubtedly, this reduced response is due to a decrease in diborane concentration brought about by the greater efficiency of the hydrolysis reaction. Thus, using the present experimental method, we cannot determine the absolute effect of humidity upon the diborane response without an analytical technique for diborane evaluation.

It is extremely doubtful that the decomposition products,  $H_2$  and  $H_3BO_3$ , are actually responsible for the response. The double release was exposed to high concentrations (1000 ppm  $H_2$ ) without effect. It is unlikely that boric acid is responsible for the effect; in fact, at the high humidities where the hydrolysis effects are greatest, higher concentrations of boric acid would be available, the response is actually diminished.

The reaction between  $NaClO_2 + B_2H_6$  has not been determined, though it has been qualitatively established that the  $ClO_2$  but no  $Cl_2$  is evolved from the  $NaClO_2$ . In this experiment a gas stream containing 100 ppm (as determined by flow meter readings) at 50% R.H. was passed through  $NaClO_2$  for 15 minutes. The effluent gas was collected in  $H_2O$  and immediately analyzed for  $Cl_2$  and  $ClO_2$ , using the spectrophotometric method of Post and Moore (ref. 18). In the sample, chlorine dioxide was found exclusively. Since the boron has been oxidized, the chlorine must disproportionate to yield as one product chlorine dioxide.

A lack of time prevented further study of the double release system. Diborane monitoring with the double release appears to be a distinct possi-

FIG. 17 DOUBLE RELEASE RESPONSE TO  $B_2H_6$



bility. The humidity variable should be investigated as should methods to detect diborane in the presence of other interferences.

Diborane was selected as being a typical member of the series; however, the response of other boranes must be evaluated. Especially important will be studies with penta- and deca-boranes which are particularly important as missile fuels.

## THE DETECTION OF BeO

### Introduction

Beryllium, the glamour element of modern technology, is capable of inflicting berylliosis, a serious disease. Inhalation of the element in any form can cause acute or chronic pneumonitis with a 30% mortality rate. No treatment or drugs are available beyond those in the research stage (ref. 19).

The toxic nature of beryllium requires that sensitive detection techniques be employed to safeguard operating personnel. AEC recommended limits are set at 2  $\mu\text{gms}/\text{meter}^3$ . The corresponding concentrations for lead, mercury, arsenic, and cadmium are 50 to 200 times greater, indicating the extreme toxicity of beryllium. Recommended concentration limits (ref. 20) for communities in the vicinity of beryllium discharges are .01  $\mu\text{gm}/\text{meter}^3$ . This is ten times the Be concentration of ordinary outdoor air.

An additional reason for accurately determining BeO might be to monitor structural component deterioration, as in rocket engines, nose cones, etc. Its high energy per unit volume (greater than any other element)(ref. 20) may result in the widespread use of Be content fuels. Extreme monitoring requirements would be required in this event.

Being a light element (Atomic No. 4) beryllium readily yields neutrons when bombarded with high energy particles. Thus, a neutron production and detection scheme for the low level measurement of BeO is suggested. The problem of choosing the proper neutron excitation and detection means which give the performance desired is discussed below. The results of a literature survey performed to ascertain the optimum techniques are presented in the Appendix.

### Neutron Excitation and Detection Techniques

High energy particles from radioactive sources are ideal for use in a field instrument. Stability is assured and predictable, power is not required, and replacement is infrequent. Compactness and simplicity are additional advantages.

Alpha and gamma bombardment have been used with much success to generate neutrons from beryllium. Gamma sources are most useful in geological field assaying because of their higher penetrability and specificity of measurement (ref. 21). In applications where gamma background is objectionable and depth of penetration unnecessary, alpha sources are far superior, provided no other



neutron-yielding elements are present. For the problem at hand, where BeO particles are to be collected and counted, these conditions are satisfied.

The reaction for the alpha bombardment of beryllium is  $\text{Be}^9 (\alpha, n\gamma)\text{C}^{12}$ . Sources of alpha radiation which have been the most commonly employed for the beryllium reaction are radium and polonium. Recently, plutonium has become available for commercial use at reasonable cost. Plutonium 239 has a stable neutron yield because of its 24,000 year half-life. This yield is lower (ref. 22) than that of a comparable strength PoBe source, but does not require the frequent time-dependent yield corrections necessary with the Polonium sources.

In summary, the optimum method in this application for the excitation of beryllium appears to be alpha bombardment using a plutonium 239 source. This should give the best performance compromise, considering neutron yield, output stability, and specificity. The low shielding requirement of alpha sources, compared to gamma sources, is an additional advantage from the standpoint of personnel safety and detector background interference. The appendix discusses this and other excitation methods in further detail.

In the reaction between energetic alphas and beryllium, both neutrons and prompt gammas are emitted simultaneously. Detection schemes have been devised (ref. 23) which employ the prompt gamma emitted as the  $\text{C}^{12}$  ground state is reached. The major drawback in the method is the gamma background. Prompt gammas from various impurities (ref. 24) (oxygen, carbon, iron, cobalt, copper, etc.) as well as natural background radiation cause this method to be less reliable than the methods for detection of the accompanying neutron (see Appendix).

Most neutron detectors are primarily sensitive to either fast or slow (thermal) neutrons. Thermal neutron detectors are usually of higher detection efficiency, since reaction cross sections in this energy region are very large. Inorganic solid scintillation detectors are somewhat more efficient than gas-filled or liquid counters, more convenient to use, and allow for discrimination against background gammas.

Two such scintillators in widespread use are europium activated lithium iodide (highly enriched with  $\text{Li}^6$ ) and boron-doped zinc sulfide in lucite. The former is a highly efficient thermal neutron detector, while the latter exhibits sensitivity to both fast and thermal neutrons. This is accomplished by combining the boron  $(n, \alpha)$  thermal neutron reaction with the proton recoil  $[\text{H}(n, n)]$  and scattering  $[\text{S}(n, p)]$  reactions of fast neutrons.

Since Pu-Be neutrons range as high as 10 MEV in energy, fast neutron detection sensitivity or moderation to thermal energy is required. Comparative response of the two scintillations crystals described above are given in Figures 18 and 19. The neutron source for both cases was one curie of plutonium (about 16 grams) alloyed with beryllium. The source was located in a large water tank. Thus the prime response was derived from thermalized neutrons. The location of the  $\text{Co}^{60}$  radiation cutoff is indicated on both curves. This is about 1-1/2 MEV, and serves as an approximate calibration for gamma pulse heights.

FIG. 18

RESPONSE OF Li I (Eu) CRYSTAL  
TO  $\text{Be}^9 (\alpha, n \gamma) \text{C}^{12}$  REACTION

Li I (Eu) 96%  $\text{Li}^6$  ENRICHED  
( $\frac{1}{2}$ " DIA X  $\frac{3}{4}$ " )

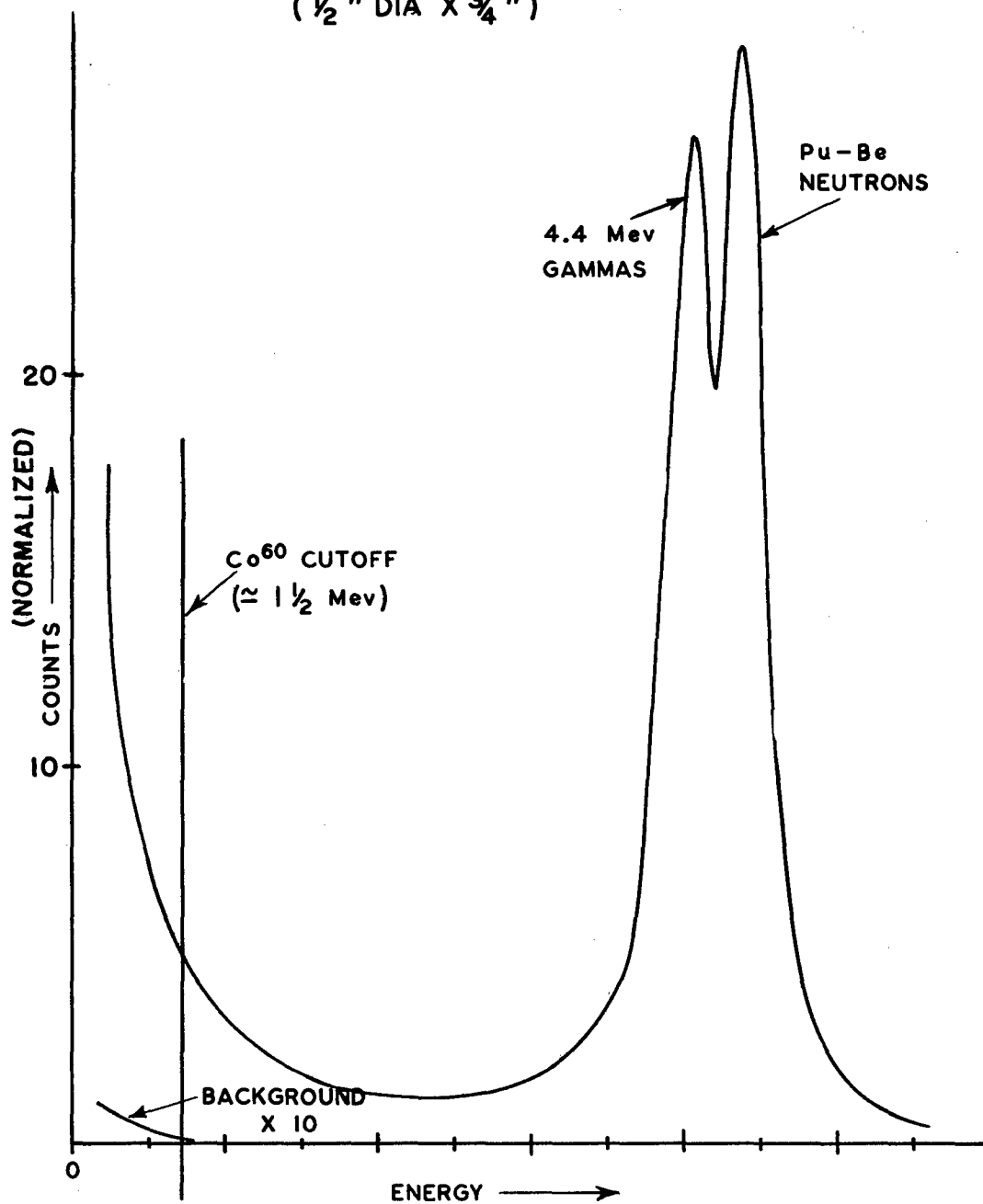
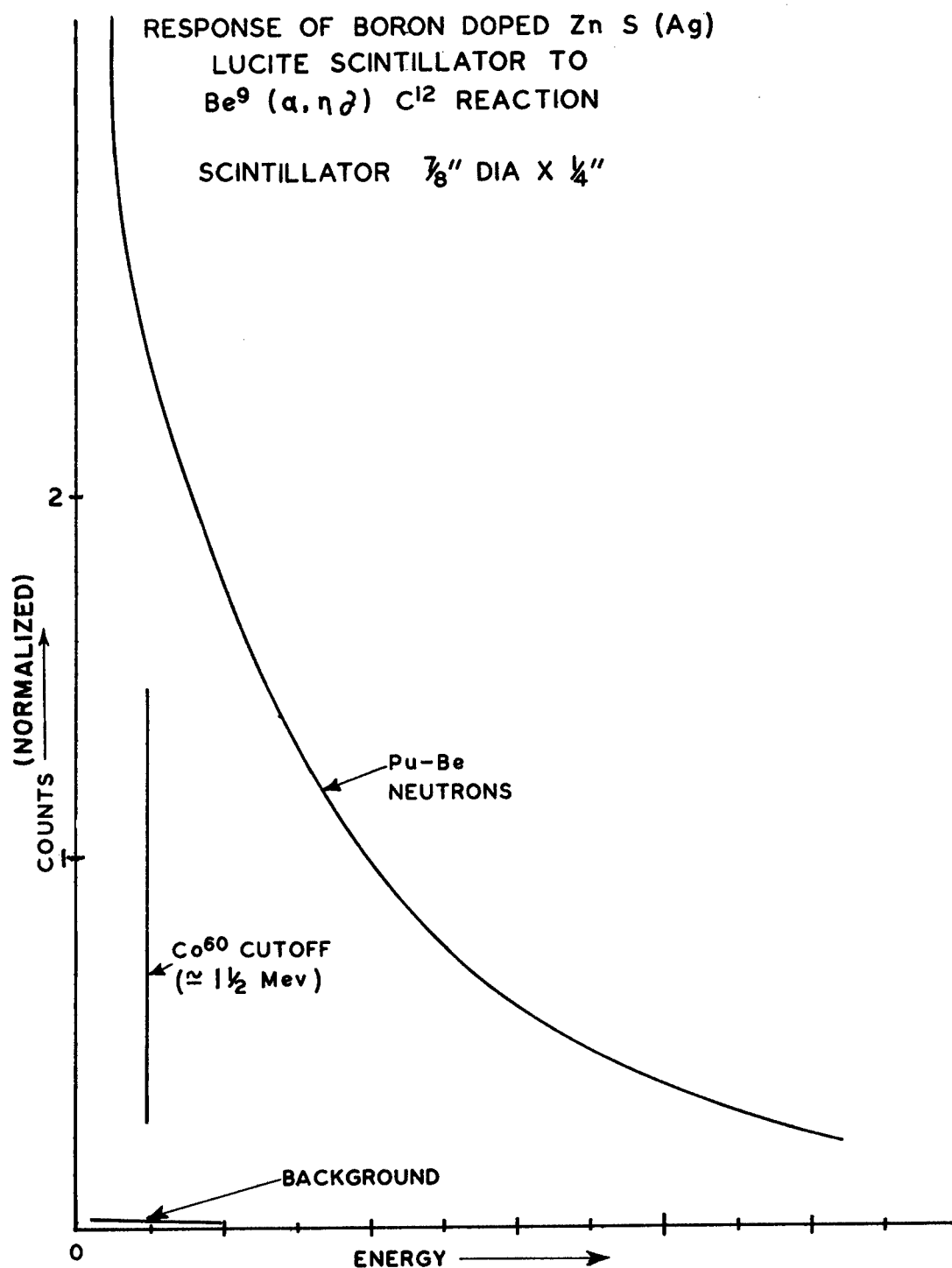


FIG. 19



A study of the two sets of data indicates that the LiI crystal is an order of magnitude greater in detection efficiency, the fast neutron response of the ZnS scintillator making a negligible contribution. The ZnS scintillator, on the other hand, is about 30% less efficient in producing gamma pulses. Considering the detection efficiency required for counting the low neutron fluxes anticipated, the LiI crystal is best suited for this application. Background gammas must be greater than 6.5 MEV to interfere with neutron counting at the peak. A NaI(Tl) crystal could be utilized, if necessary, to correct for gamma background. Preliminary laboratory data has not shown the need to correct for cosmic background.

The only other major source of background would be prompt gammas resulting from neutron bombardment of impurities. This is a possibility which must be investigated, since the collection of BeO particles in the exhaust stream may also result in the collection of structural component particles.

### Experimental Program

The selection of plutonium 239 as the alpha source, and enriched lithium iodide as the neutron detector, was the major consideration in devising a measurement scheme. For experimental convenience, it was decided to employ a weak  $\alpha$  source, which would be used to bombard a pure beryllium disc. This would avoid the necessity of handling hazardous beryllium powder, and at the same time would eliminate the necessity of obtaining a strong  $\alpha$  source, which for experimental inconvenience would have been undesirable. Details of these components and other associated apparatus are discussed below.

#### a. Plutonium Alpha Source

Plutonium alpha sources are prepared by the Mound Laboratory, Miamisburgh, Ohio. The source is  $1\frac{1}{2}$ " dia. x .060" (approx.) thick. Source strength is about  $1.9 \times 10^7$  cpm ( $\approx 8.4\mu\text{c}$ ), taking into consideration the 5 to 10% absorption from the gold plated film over the exposed plutonium.

Previous research (ref. 25) has shown that  $7 \times 10^4$  neutrons/sec per gram of PuBe are obtained. This is about 22 neutrons/sec for  $10\mu\text{c}$  of Pu<sup>239</sup>. In our experimental program, we may obtain only a fraction of this yield, since it will not be an alloy configuration. This will still give a very useable signal from which system sensitivity may be estimated.

#### b. Neutron Scintillator

Europium activated lithium iodide crystals (96% Li<sup>6</sup> enriched) are manufactured by the Harshaw Chemical Company, Cleveland, Ohio. Detection efficiency for the enriched crystal is determined from the equation (ref. 26)

$$\frac{E}{100} = 1 - e^{-\epsilon N_d}$$

where

$E$  = Detection efficiency, in %

$\sigma$  = Cross section for (n, $\alpha$ ) reaction, cm<sup>2</sup>

N = No. of Lithium Atoms/cc

d = crystal thickness (cm)

For the enriched crystal,  $N \approx 15 \times 10^{22}$  atoms/cc,  $\sigma = 71$  Barns (AT .025 ev), and d is fixed at 2 mm. Substituting these values into the above equation, we determine the efficiency of detection for every neutron entering the crystal to be  $E \approx 85\%$ .

To obtain good geometry, a crystal 1-1/2" in diameter has been procured. Although energy resolution is not of prime concern here, a lucite "light-pipe" will be coupled to the thin "pancake" crystal for this purpose. This will serve to better distribute the light scintillations over the multiplier tube photo-cathode. The lucite performs the additional function of moderating fast neutrons and reflecting some of these back into the crystal to be counted.

#### c. Neutron Source Fixture

A means for rigidly holding the alpha source and beryllium sample is necessary so that a fixed irradiation geometry is maintained during the experimental program. A simple fixture has been fabricated, and is shown in exploded view in Figure 20. The alpha source and beryllium disc are separated by a 1/16" spacer. The entire assembly is housed in a lucite case, open at the detector end only. This provides for moderation of fast neutrons that might otherwise present a radiation hazard during handling.

#### d. Instrumentation and Electronics

Detection of the light scintillations occurring in the LiI crystal (as the result of neutron interactions) is accomplished by direct optical coupling to a photomultiplier tube. These light pulses are converted into electrical impulses at a photocathode, and then amplified greatly. The amplified pulses leave the phototube and are fed to a spectrometer, where only those pulses attributable to neutron reactions are retained and further amplified.

A means of counting these "neutron" pulses is the final element in the system. For laboratory programs, a scaler (i.e., electronic pulse counter) is desirable because of its high counting accuracy. On-stream applications in the field are best read-out with a ratemeter, since changes in counting rate may be rapidly determined. Figure 21 is a block diagram of the electronic components employed in a typical detection system as described above.

#### e. Data

Data were obtained with the source and detector described above. Figure 22 is a block diagram of the experimental arrangement. Geometric efficiency of 25% ( $\pi$  geometry) was employed. Readout was accomplished with a 200 channel RIDL spectrum analyzer. Counts were accumulated overnight

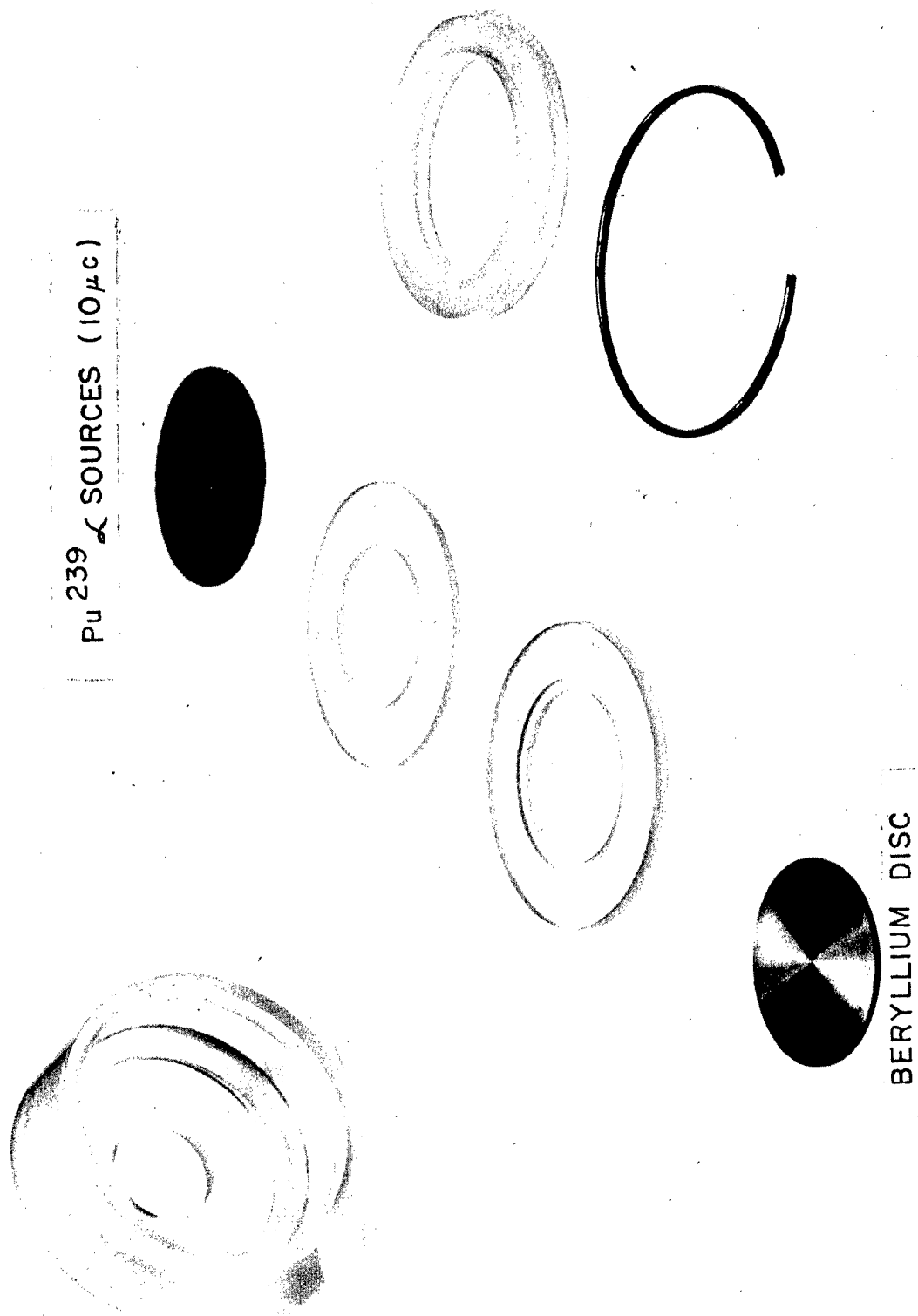


FIG. 20 NEUTRON SOURCE FIXTURE  
(DISASSEMBLED)

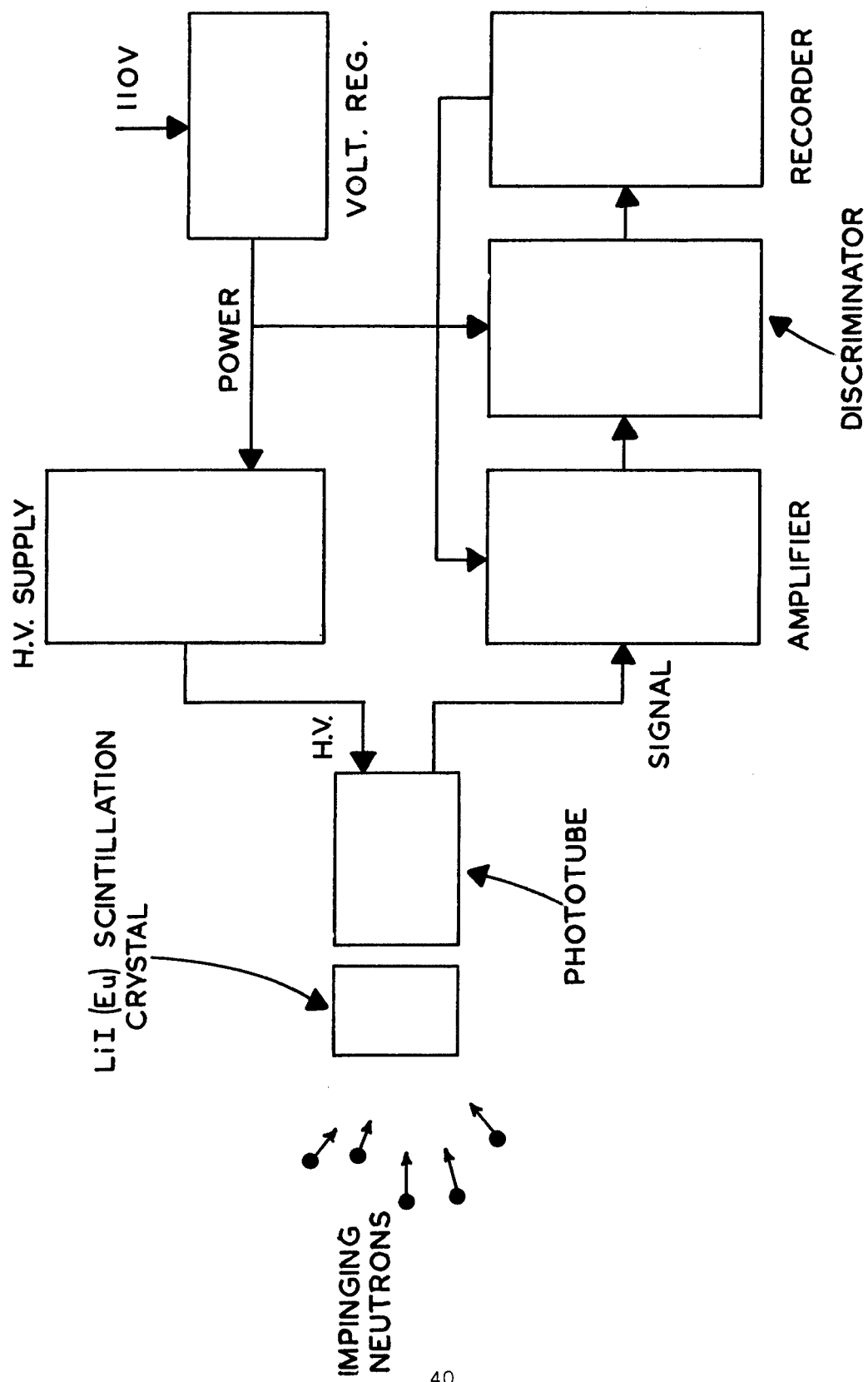


FIG. 2I BLOCK DIAGRAM OF A TYPICAL NEUTRON DETECTION SYSTEM EMPLOYING A SCINTILLATION CRYSTAL.

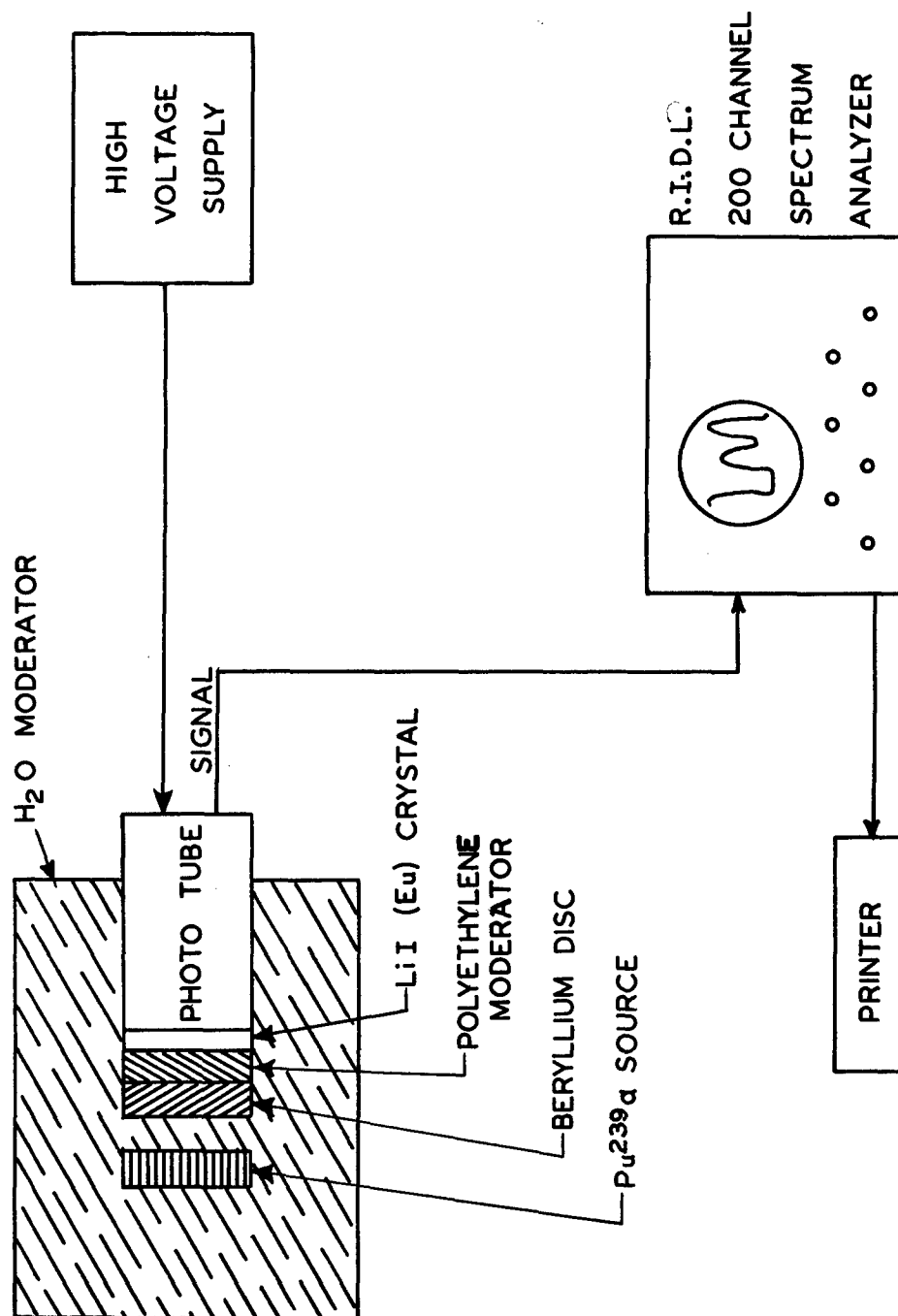


FIG.22 BLOCK DIAGRAM — EXPERIMENTAL PROGRAM INSTRUMENTATION



(16 hours) to provide good statistical data.

Spectra were obtained for conditions with and without a surrounding moderating medium (six inches of H<sub>2</sub>O in this case). These are shown in Figures 23 and 24, respectively. The large increase in thermal neutron count with moderation almost masks the counts from the prompt gamma (4.4 Mev) evident in Figure 24 (lower energy peak).

Background is indicated in each figure. The apparent increase around the neutron peak was caused by a large Pu-Be neutron source located some distance away (~150'), plus cosmic neutron bombardment. These could be substantially reduced by shielding externally with a neutron absorbing material.

Several runs with and without moderating material were conducted. The results were average and are tabulated in Table III.

TABLE III

Pu-Be Neutron Detection Data

<u>Condition</u>	<u>Avg. Time</u>	<u>Counts Avg. Gross</u>	<u>Counts Avg. Bkg'd</u>	<u>Counts Avg. Net</u>	<u>CPM/Sterad/Curie/μgm Be</u>
Moderator Surrounding Source-Detector (6" of H <sub>2</sub> O)	16 Hrs.	4350	1550	2800	0.9
No Moderator	16 Hrs.	2400	2050	350	0.1

Determination of Monitor Performance

The research of others (refs. 22, 25) has shown that about  $1.0 \times 10^6$  neutrons/sec are generated per curie of Pu<sup>239</sup> alloyed with beryllium (PuBe<sub>13</sub>).

Calculating the geometric efficiency of our alpha-bombardment technique to be one-third that of the alloy configuration, we would expect our 10 μc α source to generate

$$\frac{1}{3} \times \frac{10^6 \text{ n/sec}}{\text{curie}} \times 10 \mu\text{c} \approx 3 \text{ n/sec.}$$

Referring to Table III, it is seen that only 3 cpm were observed with a detector geometry of 25%. The large number of neutrons escaping detection (about 15 times more than those observed) must be fast and therefore undetectable with this set-up.

Assuming for the moment detection of all generated neutrons, let us calculate the number of neutrons generated per μgm of beryllium. Since 3 n/sec are generated by bombarding a solid, pure, disc of beryllium with 10 μc,

FIG. 23

RESPONSE OF LiI (Eu) CRYSTAL  
TO  $\text{Be}^9 (\alpha, n\gamma) \text{C}^{12}$  REACTION

EXPERIMENTAL PROGRAM

$1\frac{1}{2}$ " DIA X 2mm. LiI CRYSTAL

8.4  $\mu\text{C}$   $\text{Pu}^{239}$   $\alpha$  SOURCE

MODERATOR —  $\text{H}_2\text{O}$

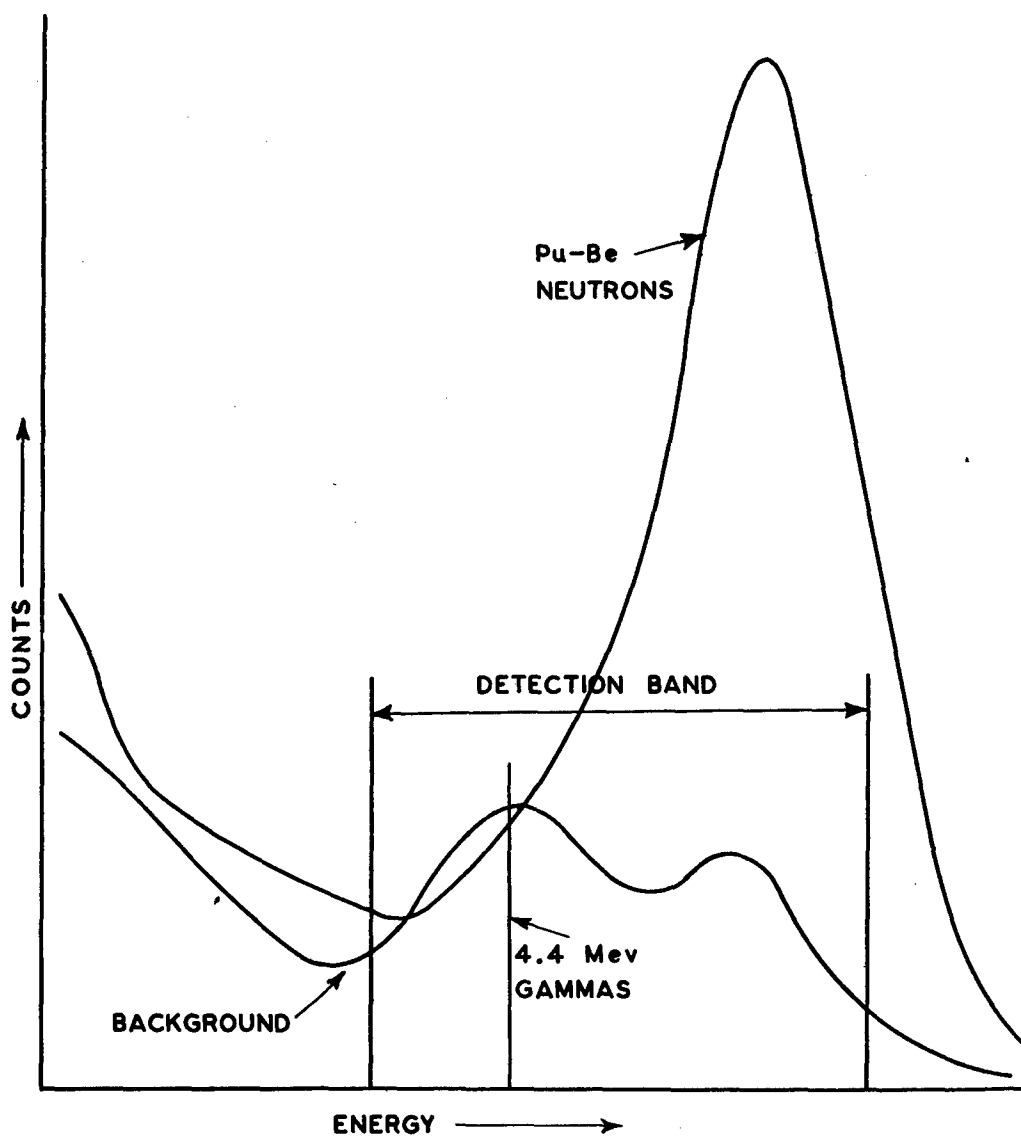


FIG. 24

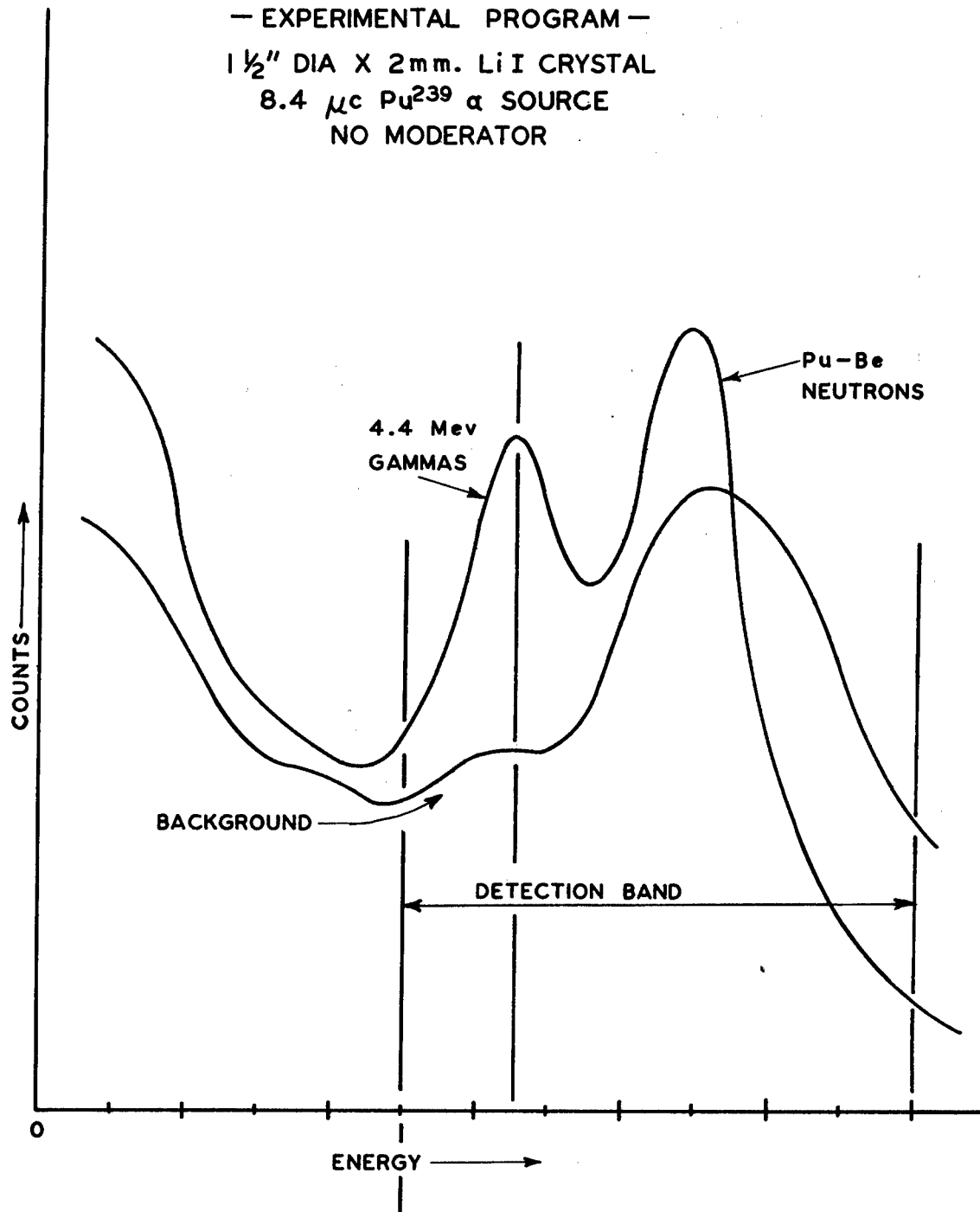
RESPONSE OF LiI (Eu) CRYSTAL  
TO  $\text{Be}^9 (\alpha, n) \text{Cl}^{12}$  REACTION

— EXPERIMENTAL PROGRAM —

1 1/2" DIA X 2mm. LiI CRYSTAL

8.4  $\mu\text{c}$   $\text{Pu}^{239}$   $\alpha$  SOURCE

NO MODERATOR



we must determine the quantity of beryllium involved in the reaction. The atomic stopping power of beryllium is 1500 times greater than that of air. Thus, if the range of  $\alpha$ 's in air from a  $\text{Pu}^{239}$  source is 3-1/2 cm, (ref. 27) their range in beryllium is  $\frac{1}{1500} \times 3\text{-}1/2 = .0023$  cm, or  $\approx .001$  inches. Now

the total weight of the .03" Be disc is 1.16 gms. The weight of beryllium interacting with the alpha particles is, therefore,

$$1.16 \times \frac{.001}{.03} \approx .04 \text{ grams.}$$

The total neutron yield using our 10  $\mu\text{c}$  source, would be

$$\frac{3 \text{ n/sec} \times 60 \text{ sec/min}}{40 \times 10^{-3} \mu \text{ gms Be}} \approx 4\text{-}1/2 \times 10^{-3} \text{ n/min}/\mu\text{gm Be.}$$

Similarly, a one curie source would yield 450 n/min/ $\mu\text{gm}$ .

The maximum  $\text{Pu}^{239}$  surface activity concentration is on the order of 2mc/in<sup>2</sup>, the limitation being a result of the self-absorption of  $\alpha$  particles. By employing three-dimensional "surfaces" of special design this figure can be increased, in effect, to activities on the order of 12 mc/in<sup>2</sup>. One such surface is an assemblage of close-packed right circular cones, of altitude not exceeding the range of  $\text{Pu}^{239}$   $\alpha$ 's in air.

The factoral increase in surface area is given by the ratio of the two areas:

$$\begin{array}{l} \text{(Rt. Circ. Cone)} \longrightarrow \frac{\pi r \sqrt{r^2 + h^2}}{\pi r^2} = \sqrt{1 + \frac{h^2}{r^2}} \\ \text{(Circle)} \longleftarrow \end{array}$$

For cones of 1-1/2 cm. altitude and 1/2 cm diameter, the factoral increase is six-fold. In terms of high activity sources, this suggests planar, or projected, areas of about 80 in<sup>2</sup> for a one curie source, although the actual total area is on the order of 500 in<sup>2</sup>.

Combining the neutron yield and activity/unit area data, an important quantity is obtained.

$$\frac{450 \text{ n/min}/\mu\text{gm Be/curie Pu}^{239}}{80 \text{ in}^2/\text{curie Pu}^{239}} \approx \frac{6 \text{ n/min}/\mu\text{gm Be/in}^2 \text{ projected}}{\text{Pu}^{239} \text{ source area.}}$$

It would be of value to consider for the moment what the above number would become if  $\text{Po}^{210}$  were employed as a source material. Having a half life about  $5 \times 10^4$  shorter than  $\text{Pu}^{239}$  (140 days vs. 24,000 years), polonium is this same factor greater in  $\alpha$  emission, or rate of radioactive decay. Thus, the above constant now becomes;

$3 \times 10^5 \text{ n/min}/\mu\text{gm Be/in}^2$  projected  $\text{Po}^{210}$  source area for one curie of polonium. The obvious disadvantage is the frequent source replacement, expense, and inconvenience (or complexity) of data correction necessary for even moderate accuracy of measurement. For those conditions, however,

where very rapid determinations are required from small sampling volumes, this source is very desirable and practical. The data presented later in Table IV forcibly illustrates the source-detector area reduction possible with  $\text{Po}^{210}$ .

From the data of Table III, the performance of a BeO detection scheme may be determined. Certain criteria of operation must first be established, however. Of primary importance are sensitivity, accuracy, and period of measurement.

Let us define the following parameters

$c = \mu \text{ grams/m}^3$  of Be in the sampled air.

$M =$  collection rate in  $\text{m}^3$  per minute.

$F =$  collection rate in cubic feet per minute.

Then

$$M = 0.027 F$$

The rate of collection of Be will be  $0.027FC \mu \text{ grams per minute}$ ;

Let  $T =$  collection time in minutes.

Then

$$S = 0.027 FCT \mu \text{ grams}$$

where

$S =$  total beryllium sample collected in the collection time.

For plutonium,

$$N_{\text{Pu}} = 60 \times S \text{ neutrons per minute generated from the collected sample (Note: assuming } 10 \text{ in}^2, 125 \text{ mc of } \text{Pu}^{239}\text{)}$$

Let  $R = \epsilon N_{\text{Pu}}$ , where  $\epsilon$  is the fraction of generated neutrons which are counted.

For a measurement time  $t$ , the total accumulated counts,  $A$ , will be

$$A = Rt$$

Since the error in the measurement is related to  $A$ , this will then be the determining factor.

Although a lower limit of  $.02 \mu\text{gm Be/m}^3$  is desirable, rapid measurements are more readily obtained by working at the accepted tolerance level of  $2 \mu\text{gms/m}^3$ . The lower limit may be determined accurately by prolonging the counting period in order to improve the statistics of the data. Many

field applications, however, will require more rapid determinations of the Be tolerance level.

Accuracy of measurement presents a similar problem. For field applications,  $\pm 5\%$  (based on a standard deviation) will usually suffice, but more accurate data can be obtained with prolonged counting, or increased source strength. Determinations of Be concentration at the tolerance level should be achieved in minutes, while concentrations at the lower limit are not required as rapidly.

The collection of particles is extremely important, since the output signal intensity is directly proportional to the amount of BeO present. Practical collection rates of 100 to 200 CFM are attainable, if 8" x 10" filters are employed. Collecting the BeO particles over this large area would require a  $\text{Pu}^{239}$  source and neutron detector of comparable area to obtain high counting efficiency. A proposed detection scheme along these lines is illustrated in Figure 25. More compact systems could be designed by employing  $\text{Po}^{210}$  as the source. The smaller area requirements would facilitate miniaturization and reduce detector size and expense. Source replacement, as mentioned previously, is the major drawback to the use of  $\text{Po}^{210}$ .

An estimate of the performances of several typical monitoring systems is of interest. To calculate the system specifications, we first assume the following:

Total neutron detector geometric efficiency ( $\epsilon$ )  $\sim 10\%$

Total neutron yield,  $Y_0 \sim 6/\text{min}/\mu\text{gm Be}/\text{in}^2$  projected area -  $\text{Pu}^{239}$  source

Be concentration,  $c \sim 2 \mu\text{gms}/\text{m}^3$  (air)

Pump collection rate,  $F \sim 100 \text{ ft}^3/\text{min}$

Pump collection rate,  $M \sim 2.7 \text{ m}^3/\text{min}$

Collection filter area = source projected area

Note that this proposed system assumes detection of 10% of all neutrons generated. This could be accomplished by locating sufficient detectors about the BeO filter, or around the moderating medium.

Tabulations are now made, for typical monitoring systems, of collection and counting periods, source strengths, and accuracy of measurement at the given conditions.

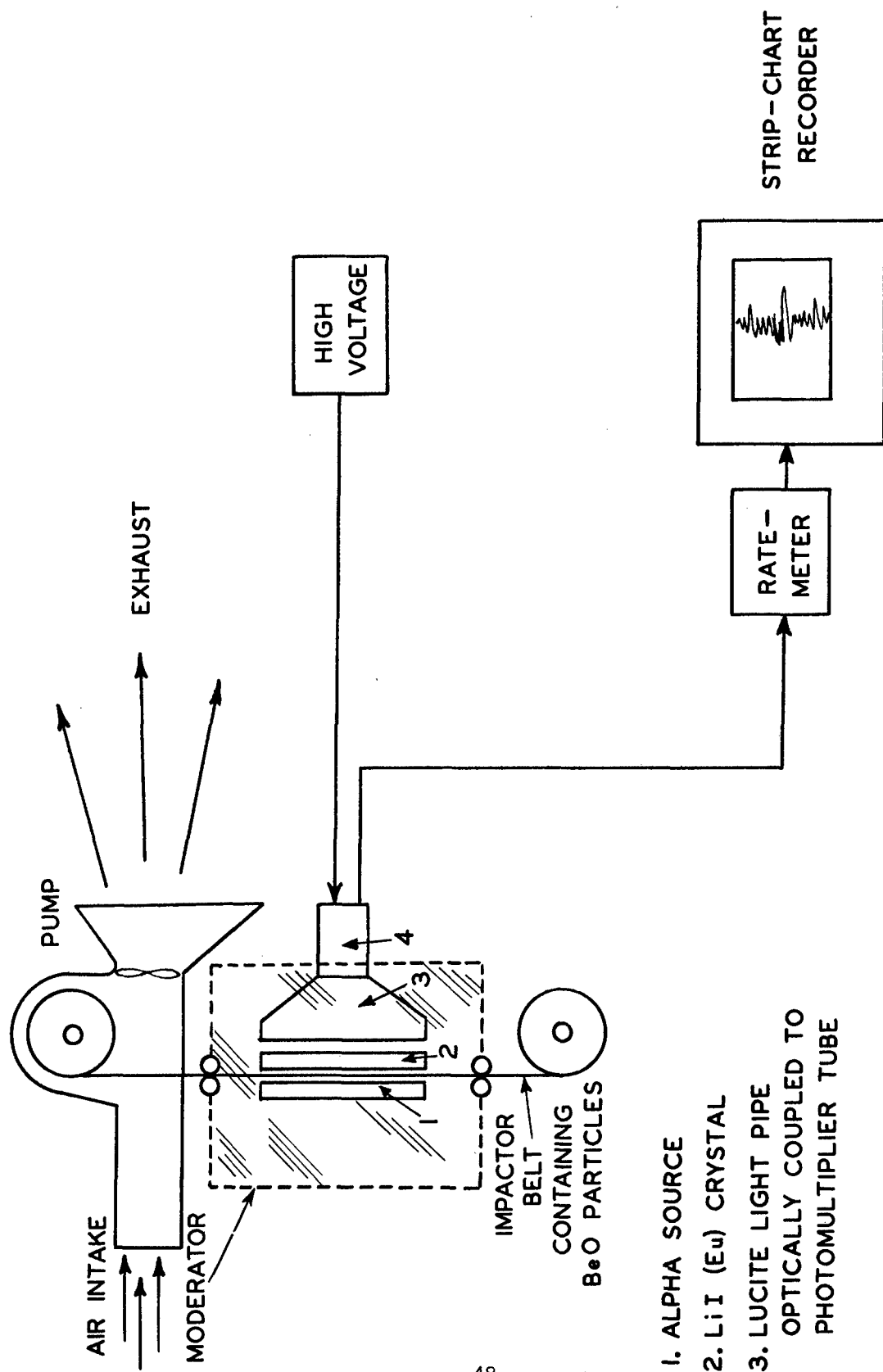


FIG.25 TYPICAL BERYLLIUM CONCENTRATION MONITORING SYSTEM

TABLE IV

Be Detection Performance Data  
for Some Typical Monitoring Systems

Isotope	Source Strength (Curies)	Source and Filter Area (in <sup>2</sup> )	Collection Period (Min)	Counting Period (Min)	Total Measurement Period (Min)	Be Accumulation (μgms)	± σ accuracy (±%)
Pu <sup>239</sup>	1	80	$\frac{1}{2}$	$\frac{1}{2}$	1	2.7	$12\frac{1}{2}$
	1	80	1	1	2	5.4	$6\frac{1}{4}$
	1	80	2	3	5	10.8	$2\frac{1}{2}$
	1	80	3	2	5	16.2	$2\frac{1}{2}$
	1	80	5	5	10	27	$1\frac{1}{4}$
	1	80	2	8	10	10.8	$1\frac{1}{2}$
	1	80	8	2	10	43	$1\frac{1}{2}$
Pu <sup>239</sup>	0.5	40	3	2	5	8	5
	0.5	40	5	5	10	13.5	$2\frac{1}{2}$
	0.5	40	2	8	10	5.5	3
	0.5	40	8	2	10	21.5	3
	0.5	40	5	10	15	13.5	1-3/4
	0.5	40	$7\frac{1}{2}$	$7\frac{1}{2}$	15	20	$1\frac{1}{4}$
	0.5	40	12	3	15	32	2
Po <sup>210</sup>	10	10	$\frac{1}{2}$	$\frac{1}{2}$	1	0.34	11
	100	10	$\frac{1}{2}$	$\frac{1}{2}$	1	0.34	$3\frac{1}{2}$
	10	10	3	2	5	2	$2\frac{1}{2}$
	10	1	3	2	5	0.2	$\frac{7}{4}$
	10	1	5	5	10	0.34	$3\frac{1}{2}$
	100	1	3	2	5	0.2	$2\frac{1}{4}$
	10	4	5	5	10	1.4	1-3/4
	10	4	10	5	15	2.7	$1\frac{1}{4}$



The above data is based on counting constant beryllium samples, such as would be obtained in periodic interval monitoring or remote laboratory analyses. The monitoring method could incorporate a continuous motion belt cascade impactor, as indicated in Figure 25. This would permit direct and rapid indications of beryllium concentration if a count rate meter were employed.

A simpler method, however, would have one filter, continually sampling air, which could be quickly placed in counting position either on command or at predetermined intervals. Upon completion of the readout, the filter would be returned to the pump and sampling continued. The data thus obtained would show a gradual build-up of BeO particles on the filter. The rate of change of this build-up is an indication of the average toxicity level for that collection period.

The particular application would determine which method is more desirable. It is not inconceivable that a monitor capable of either measurement procedure would be desirable for universal use.

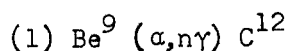
The feasibility of using nuclear techniques for determining beryllium oxide concentrations in the field has been established. Practicality of the method depends, to some extent, on the dollar expenditure allowable in order to obtain a desired accuracy and rapidity of readout. The source and neutron detector constitute the largest expense, but the useful lives of both can be made long, allowing this expense to be amortized at a low rate.

Packaging of a system must be studied in detail if the technique is to be employed in the field. Radiation safety requirements, detector shielding and power supply, moderator confinement and configuration, hurricane pump location and power, removal of dust and other particulates, and similar considerations are of much importance. The latter problem demands considerable attention, since the range of bombarding  $\alpha$ 's may not be sufficient to penetrate the dirt and dust accumulations overlaying BeO deposits on the filter. Selective filtration, perhaps employing electrostatic charge techniques, may be found necessary.

A method of changing filter characteristics, or combining several filters of varying mesh size, is of particular interest. This would readily permit a study correlating particles size with concentration, and thus provide data on toxicity levels attainable through inhalation. The use of solid-state neutron detectors also deserves investigation, since they are desirable from the standpoint of ruggedness, portability, and power supply requirements.

## Appendix

### a. Reactions



Neutron Detection. This reaction has been studied and used extensively. Sources of  $\alpha$  radiation most commonly employed are radium and polonium. Ac-Be sources have also been considered (ref. 28). Neutron yields

are high, one curie of  $\text{Po}^{210}$  yielding  $3 \times 10^6$  neutrons/sec ( $\sim 80$  neutrons/ $10^6$   $\alpha$ 's) from a thick beryllium target. Radium and its daughters (radon, Ra A, Ra C<sup>2</sup>) yield between 1/2 and twice this number of neutrons. Boron, fluorine, and lithium thick targets have yields roughly 1/3, 1/6, and 1/25 of beryllium targets (ref. 29).

An improvement in neutron source fabrication has recently been reported (ref. 30). Alloys of plutonium and beryllium are more desirable from the standpoint of neutron output stability and mechanical mixture characteristics.  $\text{PuBe}_{13}$  is resistant to oxidation and does not disintegrate into a hazardous, powdery material.

The neutron yield and energy spectrum of PoBe sources vary with the grain size of the constituents (ref. 31). These sources also require frequent time-dependent yield corrections.  $\text{Pu}^{239}$  has, on the other hand, a stable neutron yield because of its 24,000 year half-life. Its yield is lower than that of the PoBe source (ref. 31). The average energy of the  $\text{Pu}^{239}$   $\gamma$  is 5.14 Mev. Six to seven  $\times 10^4$  neutrons/sec per gram of  $\text{PuBe}_{13}$  have been measured, with the optimum concentration for neutron yield being 70% Be atoms.

The presence of  $\text{Pu}^{241}$  will cause some yield instability because of neutron growth. Sources have been fabricated with minimum quantities of this isotope.

Prompt Gamma Detection. A recent application (ref. 32) utilized the prompt gamma (4.4 Mev) emitted as the  $\text{C}^{12}$  ground state is reached. Beryllium was collected on millipore type filter paper, and then bombarded with  $\alpha$ -radiation from a 2.6 curie  $\text{Po}^{210}$  source. A 3" NaI (TL) crystal was used to obtain  $\pm 1\%$  determinations in 5 to 10 minute periods. A sensitivity of between 0.1 and 1.0  $\mu\text{gm}$  was reported.

## (2) $\text{Be}^9 (\gamma, n) \text{Be}^8$

An alternate method for producing neutrons from Be is by gamma bombardment. The threshold energy for this reaction is 1.63 Mev (ref. 33). Several isotopes are capable of significant neutron production in beryllium;  $\text{Al}^{28}$ ,  $\text{Mn}^{56}$ ,  $\text{Sb}^{124}$ ,  $\text{F}^{20}$ ,  $\text{Na}^{24}$ ,  $\text{Cl}^{38}$ , and  $\text{Ga}^{72}$ . Table V below indicates the relative worth of each of these for the production of neutrons.

TABLE V

Source Mixt.	(Barns)	Average Neutron Energy	Energy of Max. Intensity $\gamma > 1.63$ Mev.
Na+Be	5	.8 Mev	3.75 Mev
Mn+Be	11.4	.15	$\sim 1.8$
Ga+Be	8.7	.27	2
Sb+Be	18.1	.024	$\sim 1.7$
La+Be	6	.06	2.5

An instrument is commercially available from Nuclear Enterprises which uses  $\text{Sb}^{124}$  to generate neutrons from beryllium. Named the Beryllometer, it is portable and capable of making determinations in the field.

### (3) (n, $\gamma$ ) Analysis

Neutron capture (in elastic collision reaction) results in the formation of new isotopes which may be radioactive. Alternatively, the excess energy which results in the nucleus may be carried off during the bombardment by particle or gamma radiation. This "prompt gamma" reaction has been mentioned in IB.

If beryllium is used to supply the neutrons for an (n,  $\gamma$ ) reaction, a measure of the  $\gamma$ -radiation will in turn quantitatively indicate the beryllium atom concentration. Table VI lists some typical (n,  $\gamma$ ) reactions for a number of elements (ref. 34). Not included is a thermal neutron reaction with CL which gives sufficient signal to detect 50 ppm CL. A  $^{10}\text{C}$  Po-Be source and a scintillation detector have been used to obtain this sensitivity (ref. 28).

TABLE VI  
Typical (n,  $\gamma$ ) Reactions

From:

Phys. Rev. 89, 375 (1953)  
Kinsey & Bartholomew  
(AECL)

Neutron Capture  $\gamma$  rays from Ti, Cr, Fe, Ni, Zn.

Ti two strong  $\gamma$ 's, 6.7 & 6.4 Mev.

Cr 9.7 & 8.88 Mev. (13 & 35 photons, resp. per 100 captures)

Fe strong  $\gamma$  at 7.6 Mev; two weaker at 6 Mev.  
strong 9.3 Mev ( $\text{Fe}^{55}$ ); 50 photons per 100 captures.

Ni intense  $\gamma$  at 9 Mev (50% of captures); prominent  $\gamma$  at 8.5 Mev.

Zn strong  $\gamma$  at 7.9 Mev (40% of captures)

From:

Phys. Rev. 89, 396, (1953)  
Same authors as above

Neutron capture  $\gamma$  rays from Sc, V, Mn, Co, Cu.

Sc weak

V strong gammas for 7 Mev and lower. 10 photons per 100 captures.

TABLE VI (cont.)

Typical (n,  $\gamma$ ) Reactions

<u>Mn</u>	7.2 Mev; 12 photons per 100 captures.
<u>Co</u>	six gammas; each of 5% capture, about 7.5 Mev and less.
<u>Cu</u>	strong gamma at 7.9 Mev; 24% capture; another at 7.6 Mev.

## (4) (n, p) Activation Analysis

This process is not effective for low neutron energies (ref. 35). Thus the Po-Be neutrons, with an energy spectrum ranging from 1 to 11 Mev, are relatively ineffective. Silicon, aluminum, nitrogen, and oxygen have been determined with 14 Mev neutrons.

(5) (n,  $\alpha$ ) Activation Analysis

Boron and lithium yield  $\alpha$ 's when bombarded with neutrons (ref. 36).

## (6) (n, 2n)

Incident neutrons, 10 Mev or greater, may yield 2 neutrons from a bombarded nucleus (ref. 37). If the product nucleus is radioactive, it will probably be a positron emitter.

## (7) (n, 3n)

Incident neutron energies in excess of 20 Mev are required for the reaction (ref. 37), so it will not be considered.

## (8) Total Reflection

Graphite, aluminum, beryllium, copper, zinc, nickel and iron give intense regularly reflected neutron beams at glancing angles up to 10° of arc (ref. 38). These elements have negative ( $\mu-1$ ) values. Manganese behaves differently, in that its index of reflection for neutrons is greater than unity.

## (9) Photometric

The spectrophotometric determination of beryllium with 8-hydroxyquinoline has been accomplished (ref. 39). Two to 30  $\mu$ gms in 40 ml solution can be determined accurately after simple chemical preparation. A Beckman Model Du spectrophotometer was used. Some minor interference from Al and Fe impurities exist.

## (10) Fluorimetric

A fluorimetric attachment for the Beckman Model Du spectrophotometer enabled Be sensitivities of .3 to 3  $\mu$ gms to be obtained (ref. 39)

with 8-hydroxyquinaldine in 40 ml solution. Fe and Al should be removed for maximum accuracy.

### b. Practical Detection Methods

The major advantages and disadvantages of the above reactions for detecting BeO are tabulated in Table VII. Several beryllium detection schemes may be devised using one or more of these reactions. These are discussed below in order of preference from the standpoint of practicality. Table VIII summarizes this discussion.

#### Method A

The utilization of  $\text{Pu}^{239}$ ,  $\text{Ac}^{227}$ , or  $\text{Am}^{241}$  as  $\alpha$  sources appears desirable considering their output stability and non-volatility (ref. 40). Bombardment of BeO produces neutrons (1 to 11 Mev) and prompt gammas (4.4 Mev from  $\text{C}^{13}$  and 6, 7 Mev from  $\text{O}^{16}$ ).

Background counts from boron and lithium complicate neutron detection schemes. Natural gamma background and the induced activity of metallic impurities (Fe, Ni, C, Co, etc.) reduce the accuracy of the prompt gamma detection. Much of this, however, can be biased out if only the 4.4 Mev prompt gamma is used in the measurement. The activation of a gamma-emitting radioisotope, e.g.,  $\text{Al}^{28}$  or  $\text{Na}^{24}$ , would provide a signal free from prompt gamma interference.

In summary, method A can be subdivided into three detection schemes following the  $\alpha$  bombardment of Be,

1. Neutron detection
2. Prompt gamma detection ( $\text{C}^{13}$ ,  $\text{O}^{16}$ , etc.)
3. Delayed gamma detection ( $\text{Al}^{28}$ ,  $\text{Na}^{24}$ , etc.)

The major difficulty is interference from neutrons created by the bombardment of boron and lithium present with the beryllium.

#### Method B

Neutron production by  $\gamma$ -bombardment of beryllium may be used as a direct indication of Be concentration, or may induce gamma emission from a high cross-section absorber. Chlorine has a strong affinity for thermal neutrons ( $\sim 32$  barns) and yields a 5 to 7 Mev prompt gamma about 30% of the time.

Antimony-124 is a popular  $\gamma$  source for this reaction, since Be has a high cross section for the 1.7 Mev radiation. Only deuterium and beryllium have ( $\gamma, n$ ) thresholds below 5 Mev; therefore, no interfering neutrons from lithium, boron, etc., will be present. One drawback is the lower neutron yield from this reaction (about 1/15 of that from an equal intensity Po source), but the favorable neutron background condition outweighs this deficiency. An additional consideration in this method is the

shielding requirement for the energetic source gammas.

Gamma rays arising from neutron capture by metallic impurities (see Table VI) may cause some interfering background, as will natural and cosmic radiations. The extent of metallic impurities present will greatly influence the practicality of gamma detection.

TABLE VII  
COMPARISON OF REACTIONS

<u>Reaction</u>	<u>Advantages</u>	<u>Disadvantages</u>
( $\alpha, n$ )	High neutron Yields/curie	Interference from boron & lithium
$\text{Be}^9(\alpha, \gamma)\text{C}^{12}$	Good sensitivity. Rapid determ., specific	Interfering background
( $\gamma, n$ )	Possibly greater yield because of range of $\gamma$ s. Specific, since only Be yields neutrons if $\gamma \lesssim \text{Mev.}$	Low yield relative to $\alpha, n$ reactions. Interfering signals from metallic impurities prompt gammas.
( $n, \gamma$ )	Specific. Possible high yield. Good sensitivity.	Interfering background.
( $n, p$ )		Very low yield.
( $n, \alpha$ )		Probably low yield. Interference from B & Li.
( $n, 2n$ )	Neutron gain of 2.	Probable low yield due to high neutron energy requirement.
( $n, 3n$ )		Impossible for Po-Be or Sb-Be.
(Total Reflect)	Specific	Rigid mechanical requirements. High yields and high energies probably required.
Photometric	Accurate & Specific	Chemical preparation required to eliminate impurity interferences.
Fluorimetric	Accurate & Specific	Chemical preparation required to eliminate impurity interferences.

TABLE VIII  
COMPARATIVE ANALYSIS OF DETECTION METHODS

<u>Method</u>	<u>Advantages</u>	<u>Disadvantages</u>
$\text{Be}(\alpha, n)\text{C}^{12}$ using $\text{Pu}^{239}$ or $\text{Am}^{241}$	Stable output. Little shielding required.	B and Li neutron production interference.
$\text{Be}(\alpha, \gamma)\text{C}^{12}$ using $\text{Pu}^{239}$ or $\text{Am}^{241}$	Efficiency of gamma detection. Neutrons may be shielded.	Some interference from metallic impurity prompt gammas. B and Li neutron production interference.
$\text{Be}(\alpha, n)\text{C}^{12}$ using $\text{Pu}^{239}$ or $\text{Am}^{241}$ + delayed gamma by neutron activation of a target material.	No prompt gamma background. Neutrons may be shielded.	Probable low yield. B and Li neutron production interference.
$\text{Be}^9(\gamma, n)\text{Be}^8$ using $\text{Sb}^{124}$	Highly specific (No B or Li interference)	1/15 yield of equal strength Po-Be reaction. Shielding requirement.
$\text{Be}^9(\gamma, n)\text{Be}^8$ using $\text{Sb}^{124}$ + prompt gamma from $\text{Cl}^{38}$	Efficiency of gamma detection. Neutrons may be shielded.	Interference from metallic impurity prompt gammas.

#### SUMMARY AND CONCLUSIONS

Tracerlab has been engaged to investigate radiometric methods for detecting trace quantities of five typical toxic propellant gases. Proposed methods are to be practical and capable of leading to an instrument adaptable to either batch analysis or continuous flow monitoring.

Possible systems were screened and the more promising were studied in detail. Some systems were more extensively examined; this was due to the limited time available in the program so that the degree of emphasis given to a particular system was weighted against the probability of achieving immediate goals. As to be expected in a program of this nature, some of these systems proved impractical, others deserved further study, while some showed definite merit and should be capable of immediate development into useful monitoring systems.

The information obtained from this program could, with a modest effort, lead to sensitive monitoring instruments for several of the above pollutant gases. To determine the ultimate merit of other methods further study is necessary.

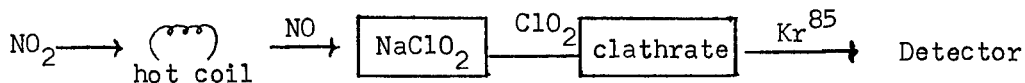
#### $\text{NO}_2$ and UDMH/ $\text{N}_2\text{H}_4$ Monitors

The results derived from the program are sufficiently positive such that recommendations can be made for their implementation into instrumentation for at least nitrogen dioxide, hydrazine and UDMH monitors.

Though a single instrument could be designed to monitor the above toxicants the basic units will be treated separately so that we will speak of an NO<sub>2</sub> monitor and a UDMH and/or N<sub>2</sub>H<sub>4</sub> monitor.

### The NO<sub>2</sub> Sensor

The physical-chemical basis for the sensor is shown in the diagram.



The hot coil which thermally decomposes the NO<sub>2</sub> into NO also destroys many other substances which may interfere with the reaction. Thus the hydrazines, for example, would be converted to non-reactive NH<sub>3</sub> or N<sub>2</sub>; and ozone would be dissociated to oxygen.

The liberated Kr-85 is counted by conventional geiger tube circuitry which is discussed below. Within measurement errors this system is quite linear (see Figure 3, pg. 5) and the statistical errors are low due to the high counting rates.

If it were desirable to differentiate between NO and NO<sub>2</sub> this would be possible by arranging a by-pass whereby NO<sub>2</sub> reacts directly and selectively with the clathrate. However, there will be some loss of specificity in this procedure since hydrazine also displays clathrate sensitivity.

### The UDMH/N<sub>2</sub>H<sub>4</sub> Sensor

The proposed system involves the following technique. The UDMH (N<sub>2</sub>H<sub>4</sub>) is passed across a hot platinum catalyst which performs a dual function. The UDMH is thermally decomposed to give ammonia as one of its by-products. Ammonia in turn is catalytically converted to NO. This is the Ostwald process which is the basis of nitric acid manufacture.



The nitric oxide is then passed through the "double release" cells previously described under the NO<sub>2</sub> monitor section.

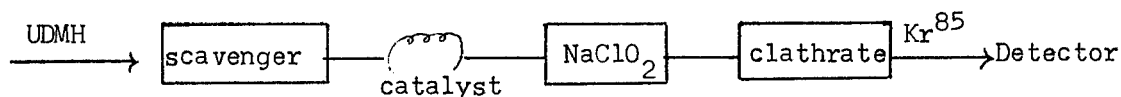
Nitrogen dioxide will give a response similar to UDMH so that means must be provided for differentiation; this can be done in either of two ways. One procedure would be to have two parallel sensors, one being the NO<sub>2</sub> sensor and the other a unit which gives a measure of the total response of NO<sub>2</sub> and hydrazines. The difference between the two signals, which is the UDMH value, is electronically registered.

The other procedure would be to incorporate a scavenging cell which adsorbs or destroys NO<sub>2</sub> selectively. A quinol clathrate containing non-radioactive krypton would be ideal for monitoring UDMH since that compound's reactivity with clathrate is very low while NO<sub>2</sub> is removed efficiently. For hydrazine monitoring this would not be desirable since hydrazine is much more reactive with clathrate than UDMH. Other scavenging compounds would have to be sought if greater selectivity is desired. For



the monitoring of missile propellant mixtures involving  $N_2H_4$  and UDMH it may be sufficient to monitor only the UDMH; because of its higher vapor pressure it would be the major component.

A schematic diagram of the UDMH sensor utilizing a scavenger cell is illustrated below.



The basic system common to both detectors ( $NO_2$  and UDMH) has displayed a humidity dependence. Control of humidity will be achieved in the following manner. The input flow stream is split into two components - one portion will flow directly through the analyzer - the second will be passed through a sulfuric acid bubbler which will be maintained at a relative humidity of 50%. Thus, the relative humidity within the flow system will always be within the limits of 30-60%. This remaining uncertainty is now eliminated as follows:

A relative humidity transducer, located in the flow line of the analyzer following the bubbler will provide a control signal to the ratemeter, adjusting the ratemeter sensitivity to correct for humidity changes (explained below) thus maintaining calibration of the response curve initially generated during calibration at a prescribed humidity. Because of the good linearity of the response curve over the concentration levels of interest, accuracy of the system over the entire range will be equally maintained.

#### Proposed Instrumentation System

##### a. General

The krypton-85 gas molecules liberated into the monitor flow line are detected with a beta counter whose negative going electrical output pulses drive a ratemeter circuit. The system time constants can be such that a response occurs in about 60 seconds for  $NO_2$  and 20 seconds for UDMH (see Figures 6 and 14). 100% of concentration reading occurs within five minutes for  $NO_2$  and 3 minutes for UDMH. The recovery times are comparable.

The UDMH and  $NO_2$  monitors are electrically and mechanically identical with the exception that an  $NO_2$  destroyer is used in the UDMH monitor flow line and, conversely, a UDMH destroyer is used in the  $NO_2$  monitor flow line. Each system, therefore, responds only to a specific contaminant. Calibration is based upon the specific fuel vapor that is to be detected.

The particular system proposed is simple and uncomplicated. The indicating and control circuitry is straightforward in design and uses a minimum number of components, increasing the overall reliability. A typical sensitivity would be 0-25 ppm  $NO_2$  and 0-25, 0-250 ppm UDMH, each system being capable of detecting one mac of the respective gas.

The UDMH system will reliably produce an alarm for concentrations down to 0.5 ppm. In the NO<sub>2</sub> system, the alarm will trigger for concentrations as low as 5 ppm. The alarm is triggered by a second ratemeter circuit operating in parallel with the indicating ratemeter. The range setting for the UDMH indicating ratemeter has no effect on the trigger level setting in the alarm ratemeter which constantly monitors the 0-25 ppm range beta counter.

The units will be designed to operate on 115-volt  $\pm$  10%, 60  $\pm$  2 cpm supply mains. A standby emergency power supply can be incorporated into each detector to permit full operating capabilities in the event the ac supply mains fail. Long life, rechargeable nickel-cadmium cells will be automatically connected to the detector during the line failure interval. They would go on charge as soon as ac power was restored. This provides complete monitoring protection, avoiding a feeling of uncertainty on the part of personnel if power should happen to fail at a crucial moment.

Solid state electronics will be used throughout. Silicon transistors provide reliable performance at the temperature ambients to be encountered at the installation sites.

#### b. Beta Counter

A pancake type counter sensitive to beta emissions will be used to detect the krypton-85 liberated by the second stage clathrate. Lead shielding will surround the counter to minimize scatter and background counts. The counter has virtually no response to gammas, and its small volume renders it insensitive to cosmic rays, resulting in an exceptionally low background counter which is essential if the system is to reliably sense the lower concentrations. The 0-25 ppm and 0-250 ppm ranges in the UDMH system involve separate beta counters to insure the required accuracy on both ranges. Only one beta counter is required for the NO<sub>2</sub> system, however.

#### c. Ratemeter

The beta counter will be provided with high voltage from a regulated supply located on the ratemeter chassis. The counter output will be capacitively coupled to the ratemeter input stage. A one-shot multivibrator circuit is triggered each time a negative going pulse is generated in the counter. The multivibrator provides uniform height and duration pulses which are fed to an integrating type ratemeter circuit having an appropriate time constant. The pulses are stored as an electrical charge in a circuit having a definite discharge time constant. The charge that is accumulated on the integrating capacitor is coupled to the output circuit. This circuit isolates the integrator from the output load terminals. The output will constitute a nominal source impedance of 1000 ohms, or less, to the twisted pair shielded cable which is to be connected thereon. A precision voltage divider will produce a dc potential equivalent to any offset voltage level required under zero contamination conditions. External loading effects from a 6000 foot line do not affect the level. However, dc resistance in the line could reduce the offset voltage at the cable termination, the extent depending upon the termination resistance. Therefore, an adjustment

can be provided to allow setting the offset, if desired, to the required level as measured at the twisted pair cable termination.

#### d. Relative Humidity Compensation

R.H. level affects the krypton-85 clathrate sensitivity as shown in Figure 4. Therefore, an electro-humidity sensor is located in the flow line to sense RH and to transmit an equivalent electrical compensating signal to the ratemeter circuits. The ratemeter multivibrators are pulse width modulated by this compensating RH signal, resulting in the correct charge on the integrator for the contaminant levels requiring detection.

The electro-humidity sensor is an electro-hygrometric circuit element which senses changes in ohmic resistance. The transducer is a processed plastic wafer - a chemically treated styrene copolymer - which has an electrically conducting surface layer that is integral with the non-conducting substrate. Changes in relative humidity cause the surface resistivity to vary. The absence of surface coatings or emulsions and the high temperature characteristics of the special styrene results in a rugged sensor which is unaffected by condensation.

Since the humidity-sensitive portion of the sensor is restricted to the surface, water vapor is sorbed or desorbed by means of adsorption; this results in a rapid speed of response to changes in RH.

#### e. Flow Rate Sensor

A flow rate sensor is utilized to determine whether or not the flow line detector system is operating properly. It will operate in the following manner:

If no toxic gas is present, the clathrate will be liberating very few krypton-85 gas molecules. The beta counter will be generating essentially no pulses for the ratemeter circuit, resulting in a zero charge condition on the ratemeter integrating circuit capacitor.

In order to test the flow rate when no contaminant is present, means are provided to artificially stimulate the clathrate to liberate krypton-85. Stimulation is accomplished by raising the clathrate cell temperature considerably above the normal value. This will heat the clathrate sufficiently to release the radioactive krypton-85 gas. If UDMH contaminant is present, the proceeding step is, of course, not necessary. The gas molecules flow past the beta counter, registering as electrical pulses that build up a charge on the ratemeter integrating capacitor. Capacitor C1 and resistor R1 in Figure 10 represent the ratemeter integrator. Under normal operating conditions the switch SW-1 is closed, allowing an identical charge to also be stored in the secondary integrating circuit. This circuit has one-tenth the capacity value of C1 and thirty times the resistance value of R1, resulting in a decay time constant which matches the flush out time of the flow line system. The network has a negligible shunt effect on the ratemeter integrator build-up time constant. The dual

cathode follower stage VI isolates the low impedance indicating meter M1 from the relatively high impedance time constant networks.

When a substantial count is registering on the ratemeter, the bypass switch is manually closed. This bypasses the clathrate output line and consequently the krypton-85 gas is flushed from the beta counter. At the same instant, switch SW-1 is opened, isolating the two integrating networks from each other. As stated earlier the decay time for the secondary integrator is calculated to match the normal flush out time for that part of the flow line subsequent to the krypton-85 as the air flow flushes the line. If, however, an air flow malfunction is present, the meter will swing away from center due to the mismatched time constants between the active ratemeter counter, and the secondary integrating network. A high reading indicates an excessive flow rate, while a low reading indicates an inadequate flow rate.

Contacts can be provided on the meter to permit a remote check on flow rate via high and low limit indicator lamps located on the master control panel. This checking system is suggested because it involves a few additional components that provide important system performance data with minimum cost.

Provisions will also be included so air flow can be remotely turned on and off to avoid unnecessary sensing element contamination during, for example, missile firing.

Suggested schematic diagrams of the proposed instrumentation are shown in Figures 26, 27, and 28. It may be noted that the sensor voltage supply, ratemeter, etc. need not be located within the console read-out unit. These can be remotely placed connected only by electric cabling, obviating the introduction of toxic gases into the console.

The prototype instruments as described above will have to be built and given an adequate program of testing. The chemical detection systems, insofar as they have been studied, give indication of being able to meet requirements. Reproducibility, stability, linearity, etc., appear excellent for periods of a few days. These studies should be extended over thirty-day intervals of continuous operation.

Time responses came very close to desired values within the uncertainties of the time required to attain steady-state concentrations within the flow line. Studies should thus be performed with flow systems designed to minimize the time response by selecting optimum flow rates, cell designs and flow system configurations.

### The Boron Hydrides

Though relatively little attention was paid to this class of compounds, the work performed with diborane make it appear likely that they will be tractable to radiological tracing techniques.

Of particular interest will be studies involving deca- and penta-borane. If these react with the "double release" systems as did diborane their moni-

**FIG.26 COMPOSITE NO<sub>2</sub> SYSTEM BLOCK DIAGRAM**

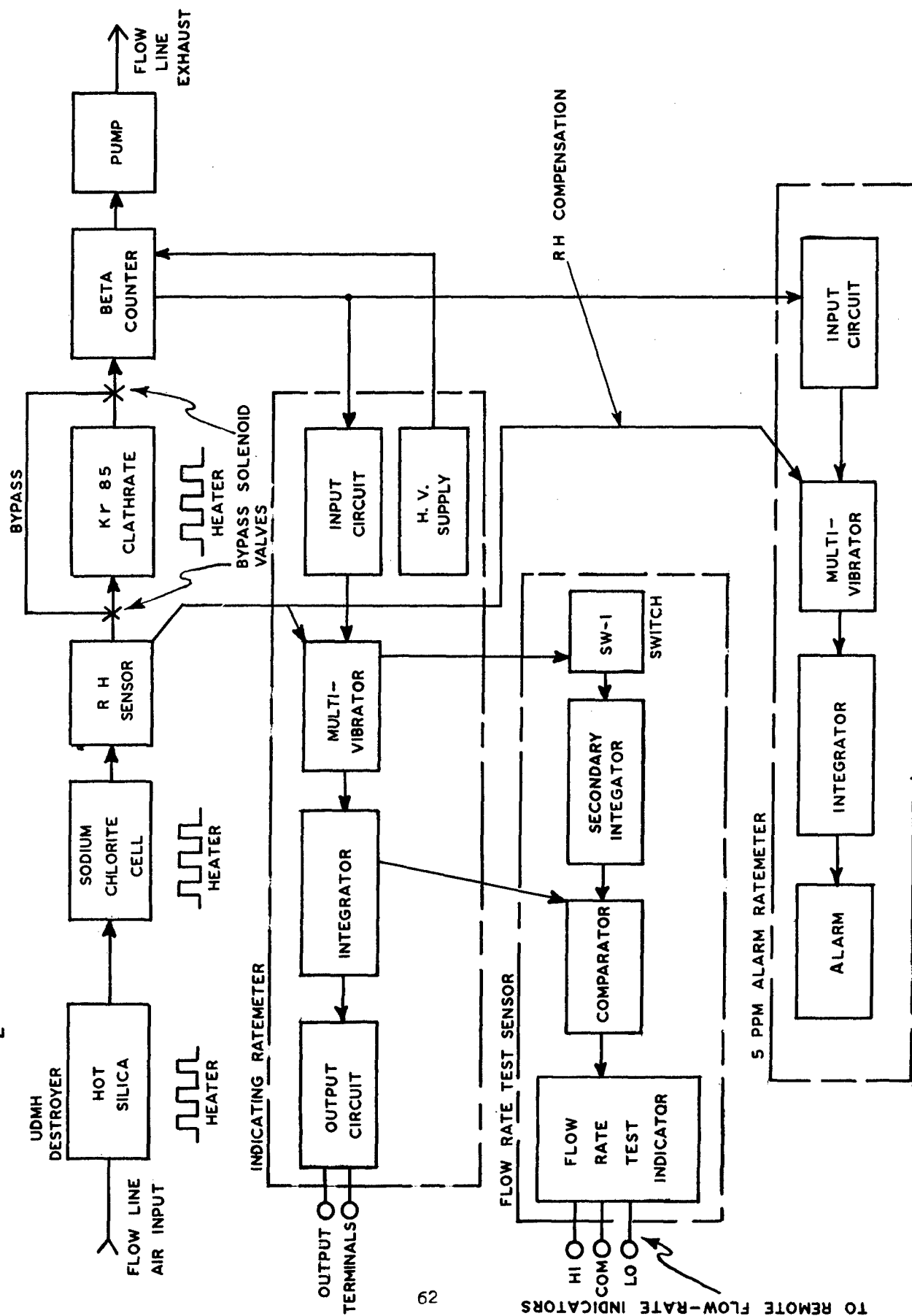


FIG. 27  
COMPOSITE UDMH SYSTEM BLOCK DIAGRAM

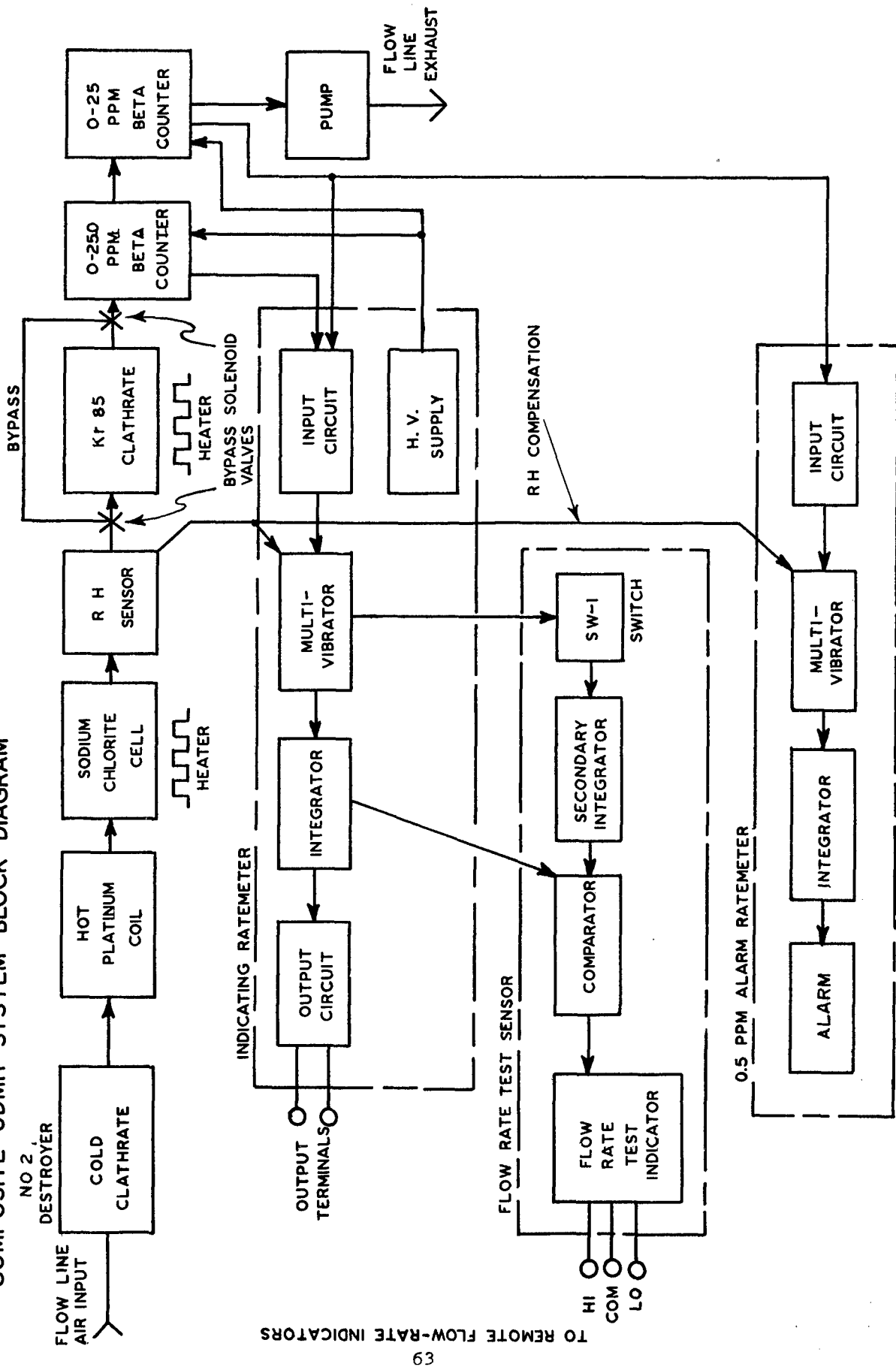
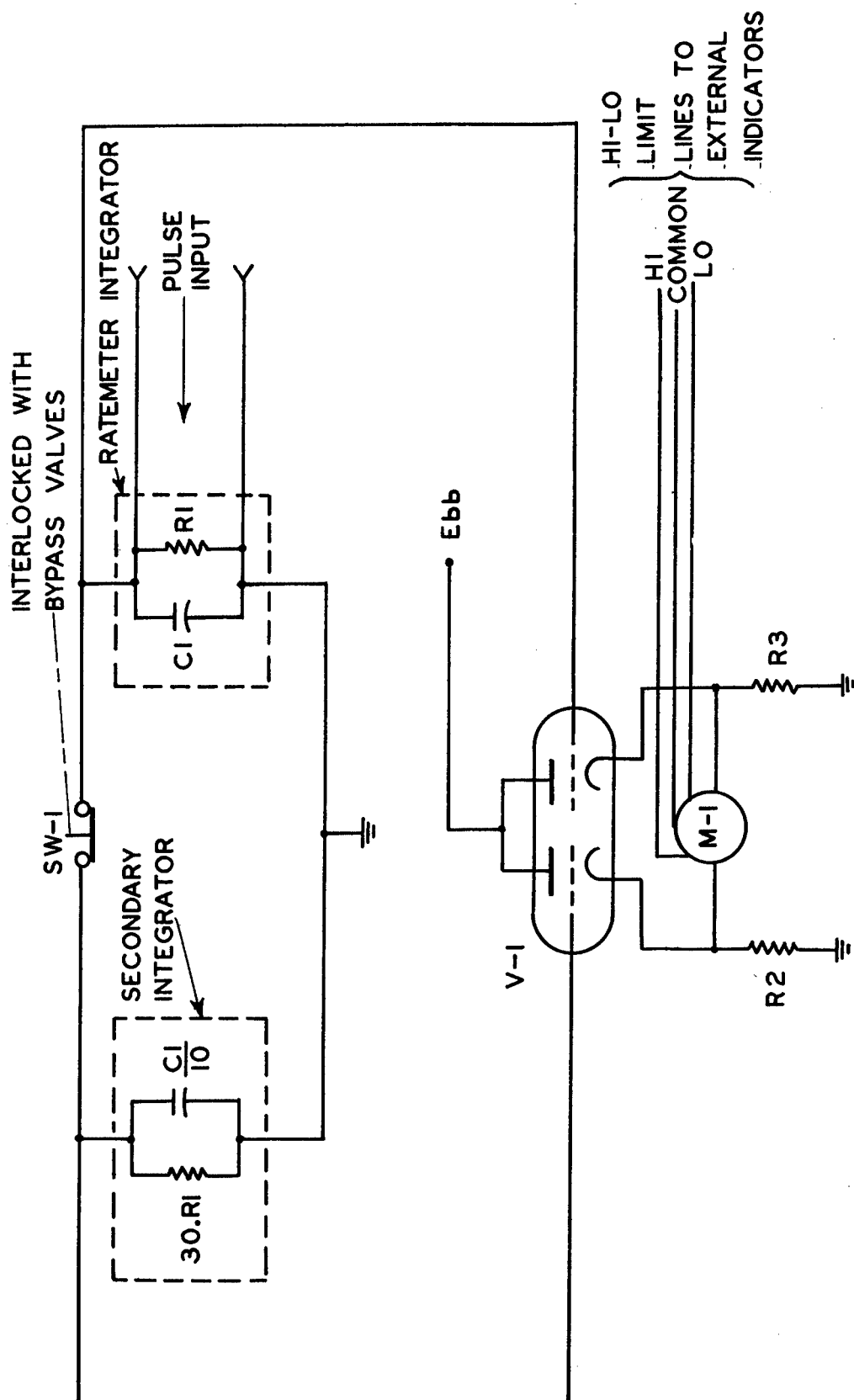


FIG. 28

FLOW RATE TEST SENSOR CIRCUIT



toring could be incorporated into the composite instrument. Methods will also have to be sought for providing specificity if it is likely that a given environment would contain these and other type missile fuels.

#### Beryllium Oxide

The detection of beryllium oxide has been investigated whereby the particulate sample is collected on appropriate filters, bombarded with  $\alpha$  rays, and the generated neutrons detected. Such a system is adaptable to continuous monitoring employing a moving filter.

Measurement of 2  $\mu$  grams Be per cubic meter is readily accomplished in a few minutes' measurement time, with a choice of a variety of configuration as described in the test. The fundamental sensitivity of the method has been demonstrated; selection of desired operating parameters for a particular monitoring application would now be required for the development of a particular monitoring system.

#### Areas for Further Development

The original program under which this work was sponsored included plans for investigating other toxic materials. These included:

Chlorine	Fluorine
Ammonia	Perchlorates
Nitric Acid	Metal Oxides

During the normal course of study much information and insight has been gained which will permit the application of radiological techniques to these other toxicants.

For example, in one study it would be found that ammonia was an intermediary produced from the catalytic decomposition of the hydrazines which in turn was converted to nitric oxide. Nitric oxide was then detected radiologically with the "double release" clathrate system. This certainly would lead one to expect that the monitoring of ammonia would be amenable to the same technique.

The other halogens, being strong oxidants, without question should respond to single or double release clathrate combinations. The perchlorates, of which the ammonium and nitronium are of particular interest, might be decomposed and treated as the oxides of nitrogen.

In retrospect it may be noted that most of the successful systems involved the use of single and double release clathrate reactions. Using appropriately placed coils to provide for operations of thermal decomposition, conversion, catalysis, etc., and the use of suitable scavenging compounds, a large range of compounds are detectable.

This suggests the development of a "block sensor" which will monitor broad classes of compounds, such as, oxidants, reductants, organics, inor-



ganics, etc. Such an instrument would have a definite appeal as a primary sensor. It would greatly simplify the identification of a toxicant and obviate the constant operation of more complex instrumentation which need only be used when dictated by the primary sensor. Another advantage would be minimum maintenance since a minimum number of monitors are in operation.

In conclusion it may be said that radiological tracing techniques are potentially very attractive and, with further development, should provide a new line of instrumentation in the field of toxic gas monitoring.

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<p>ASD TR 61-654</p> <p>Tracerlab, Inc., Waltham, Massachusetts RESEARCH ON THE FEASIBILITY OF PRO- PELLANT DETECTION BY INDUCED RADIO- ACTIVE TECHNIQUES, by F. J. Brousaides, R. Bersin, J. C. McCue, et al. December 1961. 74p. incl. illus., tables. 40 refs. (Proj. 7165; Task 716501) Unclassified report</p> <p>The feasibility of detecting small quantities of toxic propellants in the atmosphere by uti- lizing the decay characteristics of radio- active materials was studied. Activation analysis and inverse radioactive tracer tech- niques were used. The latter may be defined as processes in which a constituent to be analyzed undergoes a reaction (or reactions) (over)</p>	<p>UNCLASSIFIED</p> <p>I. Brousaides, F. J. II. Bersin, R. III. McCue, J. C. IV. Aeronautical Systems Division, Aerospace Medical Laboratory, Wright-Patterson Air Force Base, Ohio V. Contract No. AF 33(616)-7846</p>	<p>UNCLASSIFIED</p>
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<p>UNCLASSIFIED</p> <p>I. Brousaides, F. J. II. Bersin, R. III. McCue, J. C. IV. Aeronautical Systems Division, Aerospace Medical Laboratory, Wright-Patterson Air Force Base, Ohio V. Contract No. AF 33(616)-7846</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>